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TURNING WITH SHALLOW CUTS AT HIGH SPEEDS

By H. J. French and T. G. Digges

ABSTRACT

A method is described for testing lathe tools under shallow cuts and fine feeds. The relations were determined between the cutting speed, feed, depth of cut, and tool life for carbon and high-speed tool steels. Comparisons were made of tools of different forms and of tool life when cutting dry and with water or lard oil. Heat treatment and chemical composition of the tools were also studied, including, in the case of high-speed tool steels, the effects of cobalt, nickel, molybdenum, arsenic, antimony, phosphorus, sulphur, copper, tin, aluminum, titanium, and tantalum. The results obtained under shallow cuts and fine feeds with these steels are compared with those obtained under heavy duty.

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I. INTRODUCTION

Most studies of turning have been made with relatively coarse feeds and deep cuts, and it is now possible to predict, with an accuracy sufficient for many practical purposes, the cutting speeds which can be used economically in the rough turning of metals. Comparable information is not yet available for the shallow cuts used in finish turning.

The experiments described in this report relate primarily to a new method of test for lathe tools taking shallow cuts, and it was first used in a study of the effects of feed, depth, cutting liquids, and tool form upon the cutting speed to give a broad background for useful interpretation of results. The new test was then used in a study of the effect of composition and heat treatment upon the performance of carbon and high-speed steel tools and results compared with those obtained in the customary rough turning tests.

While there has recently been a tendency in machine-shop practice to replace finish turning by grinding, the discussion of a recent paper relating to the rough turning of alloy steels [1] indicated active industrial interest in test methods applicable to turning tools working at high speeds with shallow cuts and fine feeds. This is, perhaps, natural since the bulk of industrial machining does not involve cutting conditions as severe as those obtaining in the usual rough turning tests of high-speed tool steels.

II. PREVIOUS INVESTIGATIONS

It is generally believed that the methods of test developed for heavy cuts with high-speed tool steels can not be applied successfully to the shallow cuts used in finish turning. For example, Taylor [2] cautioned investigators against using "cuts lighter than 3/16 inch depth by 1/16 inch feed," and stated further that "as a result of our experience we should consider practically worthless for determining laws (of cutting) all cuts that are as shallow as 1/16 inch, and we should much prefer a 3/16-inch depth to a 1/8-inch depth."

Among the reasons for these recommendations were the difficulty of maintaining constant cutting conditions with shallow cuts, and the fact that when high frictional temperatures played only a minor part in the wear of the tools, as with shallow cuts, failure was not abrupt and complete, but, instead, the tools showed a gradual wearing away of the nose. This, of course, was reflected in a gradually changing depth of cut and raised the question of what should be considered as tool failure. Wear of the tool nose, which reduces the depth of cut by 0.001 inch, is a relatively small part of the total depth usually encountered in rough turning and is of secondary importance,

[1] H. J. French and T. G. Digges, Rough Turning With Particular Reference to the Steel Cut, Trans. Am. Soc. Mech. Engrs., **48**, p. 533.

[2] F. W. Taylor, On the Art of Cutting Metals, Trans. Am. Soc. Mech. Engrs., **28**, par. 252, p. 66; 1907.

since close adherence to dimensions is not ordinarily required. Such a change is of much greater importance in finish turning where the cuts are shallow, of the order of 0.005 to 0.010 inch or less, and where close adherence to dimensions is usually required.

The methods of test used by previous investigators for studying the gradual wear of lathe tools taking shallow cuts may be grouped under two headings: (1) Direct measurements of tool wear and (2) indirect methods of measurement.

Direct measurements of wear have been reported by Ripper and Burley [3] and Herbert.[4] In the experiments of Ripper and Burley the wear was determined by a microscope with vernier attachment. The tests, which were made in a lathe, were interrupted repeatedly to remove the tool from the holder and measure the wear.

Herbert's tests were made with a special tool-steel testing machine in which a tool was applied at the bottom end of a rotating tube placed in a vertical position. A heavy weight pressed the tube against a dead stop and regulated the amount of the cut. The vise in which the tool was held was mounted on knife-edges and tilted as the tool wore. The tilting angle of the vise was proportional to the wear of the tool and was measured by a micrometer.

Indirect methods of measuring the wear of lathe tools have been described by Poliakoff,[5] Smith and Hey,[6] and Smith and Leigh.[7]

In the method used by Poliakoff, and also by Smith and Jinoya,[8] the wear of the tools was determined from the corresponding increase in the diameter of the work (the bar being cut). An indicator was mounted on the tool rest immediately behind the tool and kept in continuous contact with the work. The tests were continued until the wear was greater than that selected to represent failure of the tool and the carriage moved back by hand, after stopping the test, to permit checking the changes in the depth of cut.

Smith and Hey and Smith and Leigh made use of a dynamometer for measuring the vertical forces on the tool when cutting. Tool comparisons were based on the time required for the vertical force to increase 10 per cent above its initial value. This increase was found to correspond approximately to a tool wear of 0.0015 inch and was stated to bear a distinct relation to the breakdown of the tool. In selecting the pressure on the tool as a measure of tool life these investigators disregarded the recommendations of Taylor and his associates who specifically stated that "no law can be established or

[3] W. Ripper and G. W. Burley, Cutting Power of Lathe Turning Tools, Proc. Inst. Mech. Eng., pts. 3 and 4, p. 1067; 1913.

[4] E. G. Herbert, The Cutting Properties of Tool Steel, J. Iron and Steel Inst., **81**, p. 206; 1910.

[5] F. Poliakoff, Cutting Tools, The Engineer, **119**, p. 275; 1915.

[6] D. Smith and I. Hey; Report of the Lathe Tools Research Committee, Department of Scientific and Industrial Research, published by His Majesty's Stationery Office; 1922; also, The Engr., **137**, p. 366; 1924.

[7] D. Smith and A. Leigh, Lathe Tool Experiments with Fine Cuts, Proc. Inst. Mech. Eng., pt. 1, p. 383; 1925, also, The Engineer, **139**, p. 318; 1925.

[8] See footnote 5.

formulated for cutting steel which expresses the relation between cutting speed and the pressure on the tool."

Some of the conclusions drawn from tests made by these different methods are compared in Table 1, which also gives a general idea of the conditions under which the tests were made. The investigators have taken different criteria for failure of the tools and have obtained what, at first glance, seem to be contradictory results. For example, Ripper and Burley found that the life of both carbon and high-speed steel tools, when represented by wear of 0.005 inch, increased as the cutting speed decreased. Most of the other investigators referred to in Table 1 found "peaks" in the cutting speed-"tool life" curves which showed that under some conditions increase in cutting speed resulted in an increase in the "tool life." Apparently, however, such critical speeds were found only when the working portions of the tools were kept at low temperatures by means of very shallow cuts and fine feeds, the use of cutting liquids, or both.

TABLE 1.—*Summary of some of the results obtained by different methods of test for lathe tools taking fine cuts*

Investigator	Criterion of tool failure	Tool steel	Metal cut	Approximate range of—	
				Feeds	Depths
				In./rev.	*Inch*
Poliakoff	0.0015 inch wear (test continued to 0.002 inch).	C and high-speed	0.35 C steel	0.014	0.0036
Smith and Jinoya.	0.001 inch wear	do	Medium C steel	.05	.003
Ripper and Burley.	0.005 inch wear	do	Mild to very hard C steels.	.0275	.020/.120
Herbert	0.001 inch wear	do	[2]	[2] 0.0012	.0625
Smith and Leigh.	10 per cent increase in vertical force.	do	0.35 C steel	.0013/.0372	.0625 and more.
Smith and Hey.	do	High-speed	do	.0013	.0625

Investigator	Coolant	Effect of cutting speed on tool life [1]	Carbon *v.* high-speed tool performance	Round-nose *v.* broad-nose tools
Poliakoff	Soap and water	Life irregular with respect to cutting speed.	C steel more durable than high-speed.	Broad-nose best for C tool steel; reversed for high-speed tool steel.
Smith and Jinoya.	Soda and water	Life increases with speed	High-speed best	
Ripper and Burley.	Tested dry	For C tool steel $V=\frac{c}{A}$ For high-speed steel: $V=\frac{K_1}{f^{1/3}-(K_2-K_3f)d}$	High-speed was about ten times as good as the C steel.	Tools with long cutting edges have longer life than those with short.
Herbert	Water in tube	Life irregular with respect to cutting speed.	At low speeds C steel more durable than high-speed steel; at high speeds this is reversed.	
Smith and Leigh.	Dry except in special experiments.	Life irregular with light cuts; decreases continuously with speed increase for heavy cuts (0.037 feed).	At low speeds C steel as good as high-speed.	
Smith and Hey.	Tested dry	Life irregular with respect to cutting speed.		

[1] V=cutting speed, f=feed, d=depth of cut, A=area of cut, and c, K_1, K_2, and K_3 are constants.

[2] Maximum obtainable.

III. PRELIMINARY TESTS WITH A DYNAMOMETER

Tests were first made with a dynamometer with the view of correlating the changes in pressure on the tools with tool wear. The dynamometer used was similar in design and construction to that employed by Stanton and Hyde [9] and is shown in Figure 1.

One of the disadvantages of such equipment, which was noted by earlier investigators, was the lack of rigidity of the test tools. Measurements of the diameter of the test forgings, subsequent to the tool tests, showed variable depths of cut from start to finish in nearly all tests. The variations were not progressive changes in one direction but appeared at irregular intervals and could be detected readily from the changes in the appearance of the cut surfaces. "Stepped cuts" were obtained in nearly all cases.

It is probable that such effects could have been minimized by refinements in the construction of the dynamometer, but since there did not seem to be any consistent relation in the preliminary tests between the vertical or horizontal forces on the tools and the tool wear the use of the dynamometer was discontinued.

IV. THE METHOD OF TEST USED UNDER SHALLOW CUTS

1. EQUIPMENT

The method of test adopted is illustrated in Figure 2. It makes use of two tools set at equal depths in one tool holder and depends upon the fact that the "trailer" or following tool will not cut so long as the "leader" or cutting tool shows no wear.

A micrometer adjustment is provided in the groove into which the trailer tool is placed in the tool holder, as is shown in Figure 3. The leader, or test tool, is first clamped securely in the tool holder, which is then moved in the direction of the depth of cut until a piece of thin (cigarette) paper can just be drawn between the work and the nose of the test tool. The micrometer adjustment is then used to bring the trailer tool into a similar position, and the trailer is securely clamped in the holder by means of the set-screws shown in Figure 3. After adjustment to equal depths the desired depth of cut is secured by setting the carriage on the lathe in the usual manner.

One of the advantages of this method of test is its simplicity, as the only special equipment required is the tool holder. Another advantage is that there is nothing to interfere with the rigidity of the test tool.

One of the disadvantages of the method is shown in Figure 4 and relates to a correction which should be applied to the observed duration of cut. If the true length of cut of the test tool L is represented by A

[9] T. E. Stanton and J. H. Hyde, Forces Exerted on the Surface of Cutting Tools. Proc. Inst. Mech. Eng., pt. 1, p. 175; 1925.

in Figure 4, then B represents the observed length of cut which differs from the true value by the amount C, representing approximately the distance between the two tools. This distance is small in relation to

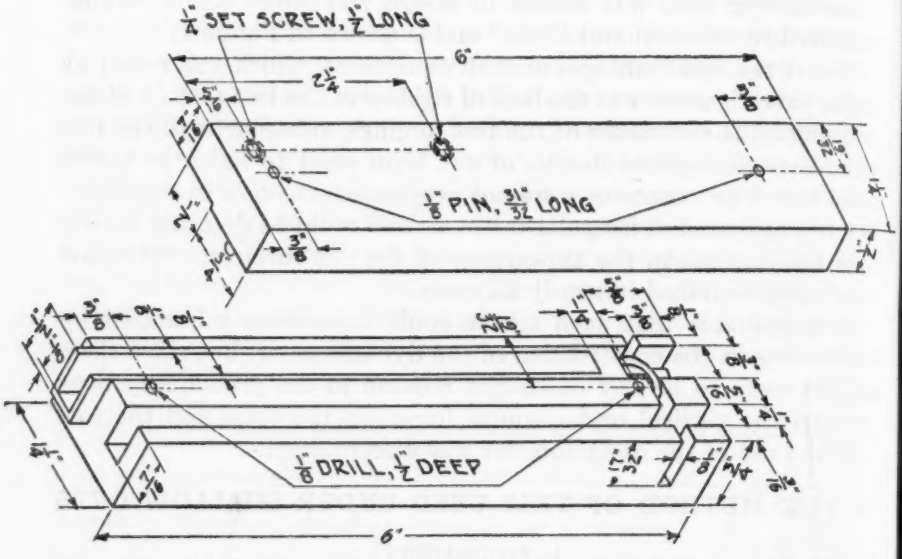

FIGURE 3.—*Details of the construction of the special tool holder illustrated in Figure 2*

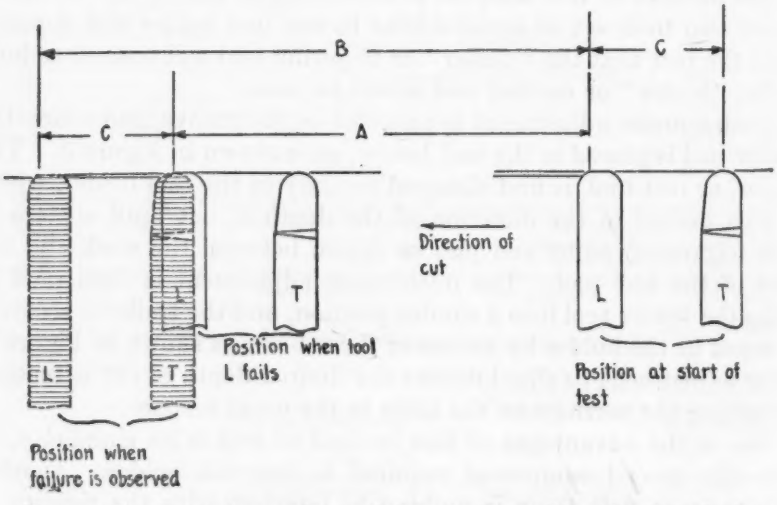

FIGURE 4.—*Corrections to be applied to the observed lengths of cut in the tests made under shallow cuts and fine feeds*

See text for discussion.

the total length of cut only when the cutting conditions permit long life. Under such conditions the correction to be applied may be neglected, since it will ordinarily be within the limits of reproduci-

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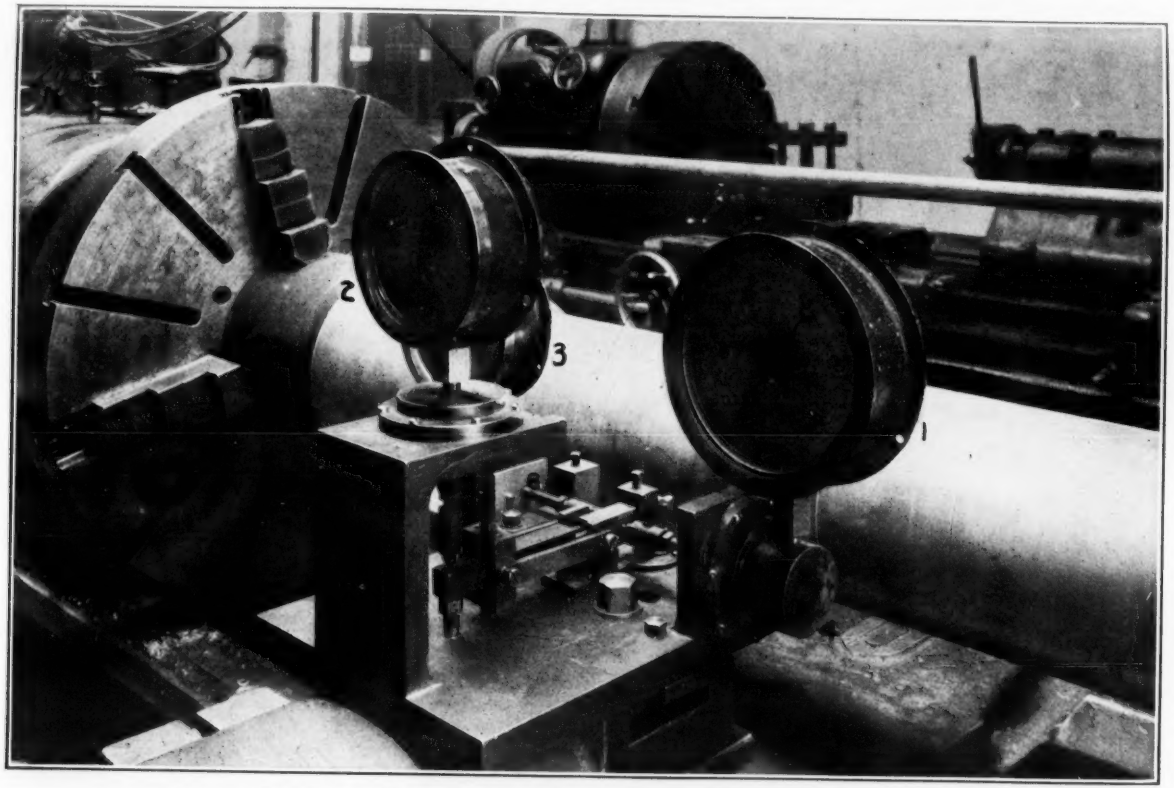

FIGURE 1.—*Force dynamometer used in the preliminary tool tests*

The vertical and horizontal forces are measured, respectively, by gage (*2*) and gages (*1*) and (*3*), acting through diaphragms, one of which, in its case, is indicated at (*4*). The diaphragms are in contact with the tool through the struts, two of which are shown at (*5*) and (*6*).

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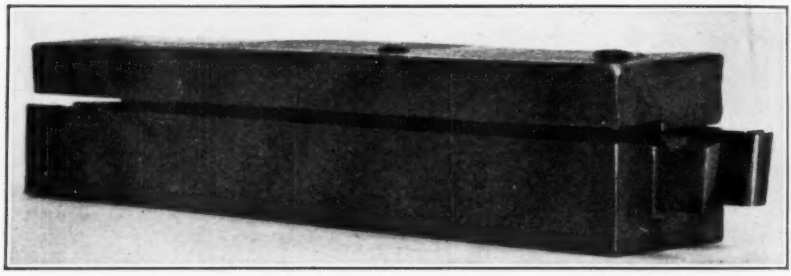

FIGURE 2.—*Special tool holder used in the tests under shallow cuts and fine feeds*

bility attained in the experiments, but the reported durations of cut have all been corrected and represent *A*, not *B*, in Figure 4. The necessary corrections of the observed lengths of cut (*B*, fig. 4) can readily be applied, since the rate of advance of the tools is readily determined from the speed of rotation of the test forging and the feed, both of which are ordinarily recorded in any turning tests.

Except when otherwise indicated, the test tool used under shallow cuts and fine feeds had a broad nose and was of the form and dimensions shown in Figure 5, *B*. A round nose tool, of the form and dimensions used in rough turning (fig. 5 *A*), was ordinarily used for the trailer.

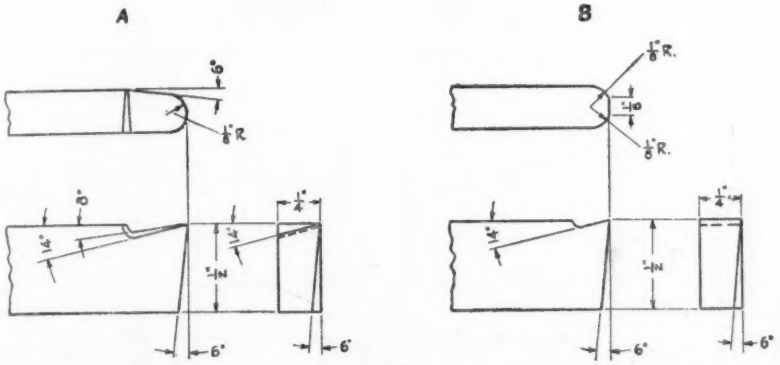

FIGURE 5.—*Forms and dimensions of the tools used in a majority of the tests*

A—Tool for rough turning. *B*—Tool for shallow cuts and fine feeds.

2. PROCEDURE

From three to six tools were tested after each of two grindings for each condition investigated, and the tests were all made in sequence. For example, in the study of the effect of cutting speed on tool performance one tool was tested at each of the selected speeds in the series, then a second tool was tested at each of the different speeds, and this procedure repeated until the desired number of tools had been tested for each condition. Only average values are used in the comparisons made throughout this report.

Testing tools in sequence has long been practiced and tends to minimize variations in results arising from inhomogeneities in the metal being cut which is seldom entirely uniform with respect to its machining properties. While this is important in rough turning, it appears to be of even greater importance with shallow cuts. Some very large differences were encountered in the tool performance at

different parts of steel forgings which showed very uniform tensile properties at different depths and from end to end.

The chemical compositions and the heat treatments of the tools used in all of the experiments except those in which a study was made of the effects of different hardening and tempering temperatures are summarized in Table 2. The compositions, treatments, and properties of the test forgings are given in Table 3.

TABLE 2.—*Chemical composition and heat treatment of tools used in tests* [1]

CARBON AND LOW ALLOY STEELS

Steel No.	Chemical composition in per cent														Quenched [1]		Tempered		Examined spectroscopically
	C	Mn	P	S	Si	Cr	W	V	Co	Ni	Mo	Ti	Ta+Cb	Other elements asspecified	From—	Into—	At—	For—	
															° F.		° F.	*Minutes*	
C14	0.76	0.38	0.041	0.033	0.05										1,450	Water	250	60	
12A [3]	.89	.39	.024	.019		0.05				0.10					1,450	do	250	60	
C2 [3]	1.09	.23	.009	.012	.19										1,425	do	250	60	
C22 [3]	1.29	.23	.017	.017	.23	.05									1,425	do	250	60	
U [3 4]	1.0	1.20				.5	0.5								1,490	Oil	250	60	
V [3]	1.34	.25	.034	.054	.32	.14	2.74								1,500	10 per cent NaCl	250	60	
HIGH-SPEED STEELS																			
CR-W-V Steels																			
E97	0.64	0.30	0.006	0.015	0.31	3.41	13.02	1.99							2,350	Oil	1,100	30	Yes.
L [3]	.71	.31	.029	.026	.24	3.60	12.75	1.99							2,350	do			Yes.
E129	.63	.39	.017	.023	.24	3.94	13.03	2.00							2,350	do			
E108	.66	.26	.027	.012	.09	3.90	18.25	1.12			0.08				2,400	do			Yes.
I [3]	.63	.29	.012	.024	.25	3.97	18.88	.81		0.15					2,400	do			
D [3]	.64	.39	.017	.017	.06	3.93	18.33	.85							2,400	do			
X [3]	.72	.21	.028	.011	.23	3.51	18.9	.90		.04					2,400	do			
E21	.70	.27	.038	.060	.44	3.79	17.90	1.01							2,400	do			
Steels with Co																			
E15	0.76	0.37	0.048	0.115	0.63	3.75	13.55	1.99	3.68	0.22					2,400	Oil	1,100	30	
A [3]	.65	.44	.013	.019	.17	4.00	14.92	1.49	3.63	.06					2,400	do	1,100	30	
K [3]	.60	.12	.008	.026	.12	2.95	18.23	.99	3.50	.09					2,450	do	1,100	30	

[1] The recorded heat treatments were used for the lathe tools unless otherwise indicated in the text of this report.

[2] The carbon steel tools were first normalized by air cooling from 1,500° F. for C14 and 12A; from 1,575° F. for C2; from 1,675° F. for C22. All high-speed steel tools were first annealed by heating for two to three hours at 1,600° to 1,650° F. and furnace cooling. They were preheated for 20 minutes at 1,600° F. and then held one and one-half minutes in the high-temperature furnace at the temperatures indicated.

[3] These steels were obtained from tool-steel manufacturers; all others were experimental melts.

[4] Type composition; purchased under trade name.

TABLE 2.—*Chemical composition and heat treatment of tools used in tests*—Continued

HIGH-SPEED STEELS—Continued

Steels with Co and Mo

Steel No.	Chemical composition in per cent														Quenched		Tempered		Examined spectroscopically
	C	Mn	P	S	Si	Cr	W	V	Co	Ni	Mo	Ti	Ta+Cb	Other elements as specified	From—	Into—	At—	For—	
															°F.		°F.	*Minutes*	
CC [3]	0.69	.017			0.34	4.23	18.32	1.53	7.8		0.96				[4] 2,375	Oil [5]	1,050	30	
Y [3]	.79	.42	0.030	0.005	.15	4.57	21.5	1.47	11.7		.61				2,400	do	1,100	30	

Steels with Mo

E109	0.61	0.18	0.027	0.009	0.04	3.34	15.44	0.81			0.74				2,400	Oil	1,100	30	Yes.
E107	.67	.23	.021	.010	.06	3.66	17.56	1.06			.85								Yes.
E31	.53	.31	.017	.023	.27	3.40	11.95	1.04			3.41								
E29	.71	.33	.013	.019	.44	4.74		.54			7.07								

Steels with Ta (+Cb)

E43	0.62	0.30	0.016	0.016	0.23	3.75	12.30	0.02					0.44		2,350	Oil	1,000	30	Yes.
E44	.66	.32	.020	.019	.25	3.65	12.20	.02					.75		2,350	do	1,000	30	Yes.
E16	.76	.35	.027	.020	.50	3.61	11.50	.06					5.08		2,350	do	1,000	30	Yes.
E45	.90	.34	.032	.021	.34	3.44	11.75	.08					2.30		2,350	do	1,000	30	Yes.
E100	1.42	.32	.007	.013	.29	3.37	13.03	.10					1.10		2,350	do	1,100	30	Yes.
E23	.69	.44	.023	.018	.55	4.28		.08					3.45		2,350	do	650	30	
E42	.69	.37	.008	.018	.44	4.23	8.17	1.58					6.05		2,350	do	1,000	30	

Steels with Ti

														Al					
E99	0.59	0.43	0.004	0.010	0.56	3.13	12.00	1.84				0.41		0.06	2,350	Oil	1,100	30	Yes.
E87	.69	.42	.024	.015	.73	3.87	11.94	1.68				1.85		.30	2,350	do	1,100	30	Yes.
E51	.80	.23	.016	.031	.41	3.89	12.90	1.96				.24			2,350	do	1,100	30	Yes.
E96	1.24	.54	.018	.015	.81	4.37	12.70	1.92				.29		.08	2,300	do	1,000	30	Yes.
E101	1.20	.45	.030	.012	.71	4.40	13.35	1.91				1.80		.38	2,300	do	1,000	30	Yes.

Steels with Al

E78	0.59	0.27	0.004	0.010	0.19	3.47	13.46	1.76						0.25	2,350	Oil	1,100	30	Yes.
E98	.57	.30	.004	.015	.28	3.35	13.10	1.97						.78	2,350	do	1,100	30	Yes.

Steels with Cu

Steels with Cu

E72	0.66	0.24	0.024	0.012	0.18	3.66	13.00	1.94						Cu 0.36	2,350	Oil	1,100	30	Yes.
E73	.65	.31	.021	.011	.18	3.61	13.15	1.92						.79					Yes.
E74	.64	.26	.021	.012	.19	3.55	12.82	1.92						1.77					Yes.

Steels with Sn

E46	0.75	0.27	0.030	0.039	0.19	3.94	12.65	1.89						Sn 0.15	2,350	Oil	1,100	30	Yes.
E47	.76	.25	.030	.039	.18	3.98	13.10	1.94						.57					Yes.
E48	.68	.22	.020	.036	.35	3.97	12.85	2.11						1.20					Yes.
E49	.69	.25	.020	.036	.32	3.98	13.10	1.97						1.85					Yes.

Steels with Sb

E77	0.60	0.28	0.025	0.011	0.14	3.63	12.94	1.81						Sb 0.41	2,350	Oil	1,100	30	Yes.
E76	.64	.50	.018	.011	.33	3.52	13.00	1.89						1.72	2,350	do	1,100	30	Yes.

Steels with As

E70	0.64	0.25	0.029	0.013	0.16	3.66	13.08	1.78						As 0.09	2,350	Oil	1,100	30	Yes.
E71	.58	.32	.030	.011	.13	3.62	12.92	1.79						.78	2,350	do	1,100	30	Yes.

Steels with P or S

E131	0.64	0.39	0.058	0.022	0.24	3.94	13.03	1.96							2,350	Oil	1,100	30	
E132	.66	.39	.020	.135	.24	3.94	13.03	1.96											
E133	.67	.39	.018	.215	.24	3.94	13.03	1.96											

Steels with Ni

E14	0.69	0.39	0.057	0.125	0.59	3.64	13.75	1.92		3.70					2,400	Oil	1,100	30	
E130	.61	.39	.017	.023	.24	3.94	13.03	1.90		3.81					2,400	do	1,100	30	
E41	.51	.27	.019	.020	.39	3.85	12.72	1.95		3.54					2,400	do	1,100	30	
E22	.61	.24	.043	.073	.55	3.66	17.40	1.02		3.71					2,450	do	1,100	30	

[1] These steels were obtained from tool-steel manufacturers; all others were experimental melts.
[2] Treated by the steel manufacturer, as follows: 1,500° F., 10 minutes; 2,375° F., 3 minutes; oil quenched.

TABLE 3.—*Chemical composition, heat treatment, and average mechanical properties of forgings cut in lathe tests (tensile test specimens taken longitudinally)*

Forging No.[1]	Chemical composition in per cent								Heat treatment	Proportional limit	Yield point	Tensile strength	Elongation in 2 inches	Reduction of area
	C	Mn	P	S	Si	Ni	Cr	Cu[2]		*1,000 lbs./in.²*	*1,000 lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*Per cent*
9	0.33	0.68	0.041	0.037	0.27	3.24	------	0.30	Exact treatment not known	62.7	----------	96.2	24.0	51.6
12	.29	.85	.032	.040	.26	2.58	------	.36	do	69.8	----------	100.7	22.5	51.0
17 and 18	.31	.56	.040	.027	.31	3.27	------	.15	1,460° F., furnace cooled	51.5	53.2	87.3	29.2	54.2
36 and 37	.40	.74	.028	.039	.24	3.32	Nil.	------	1,600° F., 12 hours air to 1,250° F., held 10 hours furnace cooled.	49.8	58.4	99.2	24.5	39.8
39	.40	.74	.028	.039	.24	3.32	Nil.	------	do	54.5	56.0	92.0	15.5	47.0
40 and 41	.34	.56	.032	.032	.21	3.30	0.05	------	1,600° F., 8 hours air cooled 1,375° F., 8 hours furnace cooled 1,150° F., 10 hours furnace cooled	42.5	48.2	82.5	29.0	49.5
42[3]	.36	.68	.023	.039	.24	3.46	.07	------	1,650° F., 10 hours air cooled 1,300° F., 10 hours furnace cooled 1,315° F., 10 hours furnace cooled 1,175° F., 10 hours furnace cooled	----------	49.2	87.5	25.6	51.0

[1] Where 2 forging numbers are given together the forgings were made from 1 heat of steel and tensile tests were made on only one of them.
[2] Copper was not determined for forgings Nos. 36, 37, 39, 40, 41, and 42.
[3] Tensile-test data reported by the manufacturer.

FIGURE 6.—*New tool and tools which failed in the tests under shallow cuts and fine feeds*

E71–8 is a new tool; E47–4 used at 400 ft./min. with 0.010 inch depth and 0.0115 in./rev. feed on test forging No. 40; L51 used with 0.005 inch depth and 0.0154 in./rev. feed at 400 ft./min. on forging No. 40.

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3. HOW CARBON AND HIGH-SPEED STEEL TOOLS FAILED

With the broad-nose tools used in the experiments, the leading edge first showed wear and the crumbling or wearing away of the nose then progressed from the leading edge to the trailing edge. This shift in the working portions of the tool from the leading to trailing edges took place slowly and could be followed quite readily in the case of most of the high-speed steel tools. It occurred more rapidly in the carbon steel tools, which generally were ruined very soon after the leading edge showed evidence of crumbling or spalling.

In the tests with high-speed steel tools a groove was formed on the top surface of the tool near the leading edge, and vertical grooves were also formed on the face, as is shown in Figure 6. The spacing of the grooves on the face corresponded to the feeds employed in the tests, and the length of the grooves was dependent upon the depth of cut. A depression or groove was also formed on the top surface of the carbon steel tools, but there was often no evidence of the feed grooves on the face after failure. When visible, the feed grooves in the carbon steel tools were not so marked as in the high-speed steel tools.

With the method of test employed, the trailer tool indicated when the leader or test tool had worn enough to produce a measurable change in the depth of cut. Experience showed that the trailer began to cut when the wear of the leader was between about 0.001 and 0.002 inch, and this was considered as the point of failure of the test tools. These values apply to tests in which the two tools are originally set at equal depths, but it should be recognized that the wear representing failure may be increased by using originally a shallower setting for the trailer than for the leader. The test is therefore applicable to a wider range of conditions than those used in the experiments.

When the tools failed in a short time, it was found that wear of 0.001 or 0.002 inch was concomitant with a complete breakdown of the tool comparable to that found with deep cuts in rough turning. In other words, the nose was rubbed off to a sufficient depth to decrease the depth of cut appreciably. (See Tables 4 and 5.)

This manner of failure was characteristic of both carbon and high-speed steel tools but, as already pointed out, this end point was reached at different rates in the two steels. The carbon steel tools failed almost immediately after the leading edge of the tools showed wear, whereas the high-speed steel tools frequently continued for some time thereafter to take a full cut.

When the tools failed completely by rubbing off of the nose, a glaze was produced on the test forging just as in the rough turning tests and gave an additional indication of failure.

TABLE 4.—*Effect of cutting conditions on the amount of wear of the high-speed steel tools at the time at which they were considered to have failed* [1]

Cutting speed (ft./min.)	Feed	Depth of cut	Area of cut	Tool steel [2]	Number of tools tested	Average tool life	Average decrease in depth of cut at failure
	In./rev.	*Inch*	*Sq. in.*			*Minutes*	*Inch*
400	0.0115	0.005	0.000058	E97	5	25.0	0.0010
	.0132		.000066		5	21.7	.0025
	.0142		.000071		5	24.6	.0023
	.0154		.000077		5	23.3	.0013
	.0204		.000102		5	19.9	.0010
350	.0115	.010	.000115	E97	5	56.8	.0055
	.0132		.000132		5	58.5	.0060
	.0142		.000142		5	42.5	.0070
	.0154		.000154		4	44.6	.0093
	.0204		.000204		5	25.1	.0070
380	.0115	.015	.000162	E97	4	19.5	.0135
	.0132		.000198		4	11.6	.0125
	.0142		.000213		5	5.4	.0128
	.0154		.000231		5	5.4	.0133
	.0204		.000306		5	2.6	.0150
400	.0115	.020	.000230	E97	5	4.1	.0175
		.015	.000162		4	12.3	.0130
		.010	.000115		4	27.6	.0060
		.005	.000058		5	36.3	.0015
350	.0204	.020	.000408	E97	5	2.4	.0195
		.015	.000306		5	5.7	.0135
		.010	.000204		4	21.4	.0065
		.005	.000102		4	38.9	.0015
300	.0115	.020	.000230	E97	5	125.5	.0120
350					5	28.2	.0175
400					5	7.5	.0165
450					5	1.6	.0170

[1] Tests were made on forging No. 40 (Table 3) with tools of the form and dimension shown in Figure 5, *B*.
[2] Composition and heat treatment given in Table 2.

TABLE 5.—*Effect of cutting conditions on the amount of wear of 1.3 per cent C steel tools at the time at which they were considered to have failed* [1]

Cutting speed (ft./min.)	Feed	Depth of cut	Area of cut	Tool steel [2]	Number of tools tested	Average tool life	Average decrease in depth of cut at failure
	In./rev.	*Inch*	*Sq. in.*			*Minutes*	*Inch*
125	0.0115	0.010	0.000115	C22	1	9.4	0.0045
115	.0142		.000142		1	10.8	.0030
110	.0154		.000154		1	7.5	.0055
91	.0204		.000204		1	35.9	.0055
90	.0204		.000204		1	55.2	.0040
160	.0115	.005	.000058	C22	1	11.4	.0030
103	.0115	.015	.000162	C22	1	10.3	.0120
95	.0115	.020	.000230	C22	1	10.0	.0060
75	.0154	.020	.000308	C22	1	13.9	.0210
65	.0204	.020	.000408	C22	1	11.6	.0165
87	.0204	.010	000204	C22	1	88.2	.0070
65	.0204	.020	.000408	C22	1	74.4	.0055
160	.0115	.005	.000058	C22	2	37.5	.0030
163					1	1.9	.0050
165					1	3.2	.0025
165	.0115	.005	.000058	12A	1	12.9	.0025
160	.0115	.005	.000058	C14	1	1.0	.0055
165					1	24.1	.0025
163	.0115	.005	.000058	C2	1	2.5	.0025
165					1	0.5	.0030

[1] Tests were made on forging No. 41 with tools of the form and dimensions shown in Figure 5, *B*.
[2] Composition and heat treatment given in Table 2.

When the cutting conditions permitted the tools to cut for only a short time, the selected method of test gave an end point which was concomitant with complete failure of the tool, and the trailer tool became unnecessary. Under more nearly practical conditions, when the tools continued to cut for long periods, the wear on the nose of 0.001 or 0.002 inch was seldom concomitant with complete failure. Under such conditions it became impracticable to determine the time of failure without an indicator, such as the trailer tool. Tests of very short duration, which might be made in the ordinary manner, even with shallow cuts and fine feeds, are of doubtful value unless it is practicable to develop at least approximate relations between such short-time tests and the long-time cutting required in practical service. Therefore, a study was made of the effects of speed, feed, and depth of cut on the durations of cut.

V. EFFECT OF CUTTING SPEED ON TOOL LIFE

1. FOR HIGH-SPEED STEEL TOOLS

The results of tests at different cutting speeds with a feed of 0.0115 inch per revolution and depths of 0.010 or 0.020 inch are summarized in Figure 7 and show that there was a continuous increase in the life of high-speed steel tools as the cutting speed was decreased. Within a life range of from 2 to 125 minutes, the experimental results may be represented by the equation

$$VT^n = c \tag{1}$$

in which V is the cutting speed in feet per minute, T the tool life in minutes, and n and c are constants.

In one of the two sets of tests summarized in Figure 7, the experimental results were most closely represented by equation (1) when n was $\frac{1}{10}$, while the best representation in the second set was obtained when n was $\frac{1}{12}$.

When taking shallow cuts with high-speed steel tools, Ripper and Burley [10] found that the relation between the cutting speed and tool life could be represented by equation (1) with n equal to $\frac{1}{12}$. They did not report the actual values of tool life, but a study of the points plotted in their charts showed that only in some cases were the relations between cutting speed and tool life best represented by equation (1) with $n = \frac{1}{12}$; in others, as good or better representation was obtained with $n = \frac{1}{10}$.

The value of the exponent n in equation (1) can not be definitely established at this time. The value $\frac{1}{10}$ was selected for use in this investigation since it is closer than $\frac{1}{12}$ to the exponent in a similar equation, which Taylor demonstrated was applicable to conditions of

[10] See footnote 3, p. 831.

rough turning. However, either of the quoted values should give results sufficiently accurate for practical purposes except when extrapolating to very long-time cutting from tests of relatively short duration.

2. FOR CARBON STEEL TOOLS

The change from very short life to very long life in carbon tool steels was most often produced by decreases of less than 5 feet per minute in the cutting speed. In the majority of the cases investigated if the tools did not fail in less than 5 minutes they continued to cut for 90 minutes without sign of failure.

In general, the tests were stopped after 90 minutes, but in a few cases tools which did not fail in this time were allowed to continue to

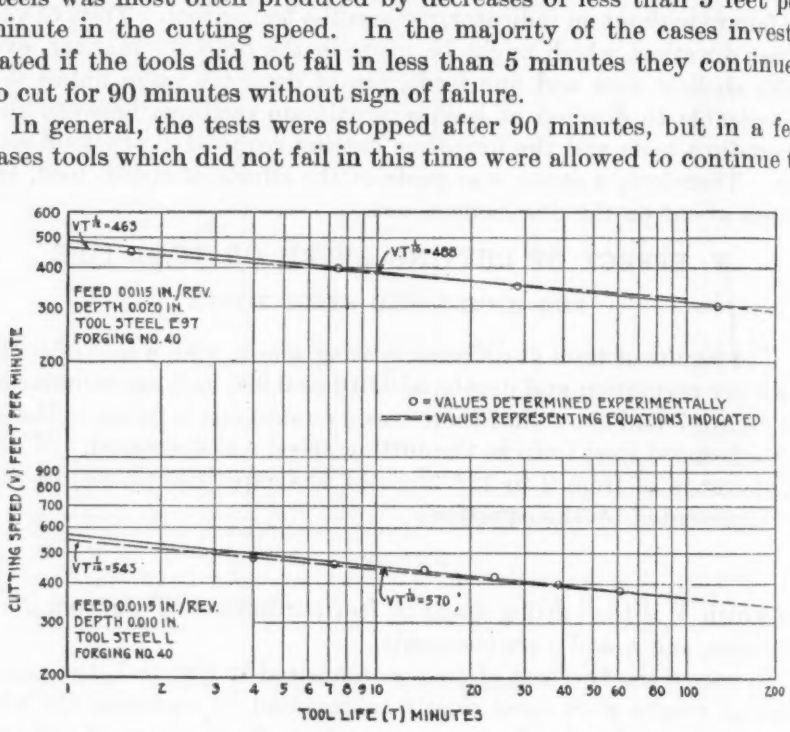

FIGURE 7.—*Relation between the cutting speed and the tool life under shallow cuts and fine feeds*

Tests made dry

cut for another 90 minutes (total time of cutting, 3 hours) without indication of failure. This, together with the general character of the cutting speed-tool life curves indicated that carbon-steel tools which cut for 90 minutes would, in general, cut for much longer periods, such as are desired in practice.

The highest speed at which the tools would cut for 90 minutes without failure was considered to represent a "critical cutting speed." It was determined by testing individual tools at successively lower cutting speeds, which differed by 2 to 5 feet per minute, until a 90-minute cut was obtained without failure.

The critical cutting speeds discussed in this report are not equal to the speeds permitting exactly 90 minutes' tool life, but, due to the sharp increases in life with decrease in cutting speed, they are so close to the latter that the two may be considered to be the same for practical purposes.

The sharp decrease in life with increase in cutting speed in the case of carbon-steel tools is probably associated with the temperatures generated at the working portions of the tools. Increase in cutting speed means increase in working temperatures, and carbon steels are known to lose hardness more rapidly with temperature rise than high-speed tool steels. The gradual change in tool life in high-speed steels is probably associated with a gradual loss in hardness, with rise in temperature resulting from increase in either cutting speed, feed, or depth of cut.

VI. EFFECT OF FEED AND DEPTH OF CUT ON CUTTING SPEED

1. FOR HIGH-SPEED STEEL TOOLS

A summary of the experiments with high-speed steel tools cutting under different feeds and depths is given in Figure 8. The relations between the cutting speed for a given tool life, the feed and depth of cut, may be represented approximately by the equation

$$V = K_1 - K_2(DF) = K_1 - K_2A \qquad (2)$$

when V is the cutting speed, D is the depth of cut, F is the feed, A is the area of cut ($=DF$), and K_1 and K_2 are constants.

With the tools and test forgings used in the experiments, as recorded in Tables 2 and 3, and a selected tool life of 90 minutes, equation (2) becomes

$$V = 370 - 32\ DF \times 10^4 \qquad (3)$$

For a selected tool life of 20 minutes and otherwise comparable conditions equation (2) becomes

$$V = 430 - 38\ DF \times 10^4 \qquad (4)$$

In equations (3) and (4), V is expressed in feet per minute, D in inches and F in inches per revolution.

Some of the plotted points are at some distance from the lines representing equation (2) in Figure 8, but Table 6 shows that the variations between the plotted points and the values given by equation (2) were within about ± 6 per cent. This is within the limits of reproducibility of the experiments and is as close concordance as may be expected. As already indicated, appreciable variations were encountered in the cutting properties from point to point in the

large test forgings. Likewise, only minor variations from the intended depths of cut in setting the tools in the lathe represent a

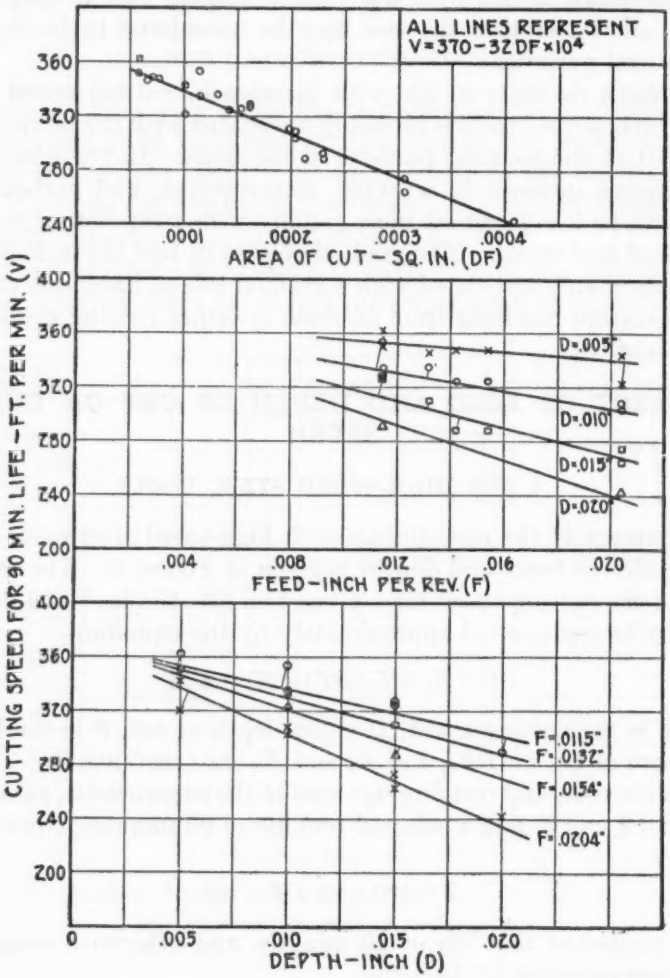

FIGURE 8.—*Effect of feed and depth of cut and the area of cut on the cutting speed of high-speed steel tools when taking shallow cuts at fine feeds*

All tests were made dry with tool steel E97 (Table 2) on forging No. 40 (Table 3).

large percentage variation with the shallow cuts under investigation, and, hence, have a relatively marked effect upon the observed tool life so that reproduction of results becomes difficult.

TABLE 6.—*Effect of feed and depth on performance of high-speed tool steel* [1]

Speed (ft./min.)	Feed	Depth	Area of cut	Tool life (minutes) 1	2	3	4	5	Average	20-minute cutting speed (calculated from $VT^{1/10}=c$)	90-minute cutting speed (calculated from $VT^{1/10}=c$)	90-minute cutting speed (calculated from $V=370-320{,}000DF$)	Difference between last and next to last columns in ft./min.
	In./rev.	*Inch*	*Sq. in.*							*Ft./min.*	*Ft./min.*	*Ft./min.*	
400	0.0115	0.005	0.000058	30.5	26.6	22.2	24.9	20.7	25.0	410	351	351	0
	.0132		.000066	18.3	25.7	19.1	19.7	25.9	21.7	405	346	349	+3
	.0142		.000071	21.1	26.9	23.0	24.2	28.0	24.6	407	348	347	−1
	.0154		.000077	25.4	22.3	28.4	22.1	18.4	23.3	406	347	345	−2
	.0204		.000102	25.5	16.1	17.3	20.8	19.8	19.9	400	342	337	−5
350	.0115	.010	.000115	54.1	59.5	58.6	51.3	60.4	56.8	385	334	333	−1
	.0132		.000132	49.0	62.4	60.1	66.8	54.0	58.5	390	335	328	−7
	.0142		.000142	56.5	43.6	37.6	38.2	36.5	42.5	375	324	325	+1
	.0154		.000154	42.6	45.2	-----	49.5	41.2	44.6	378	325	321	−4
	.0204		.000204	21.9	31.2	34.8	15.0	22.6	25.1	360	308	305	−3
380	.0115	.015	.000162	19.1	-----	12.1	30.7	16.2	19.5	379	326	318	−8
	.0132		.000198	16.9	-----	9.5	9.4	10.7	11.6	360	310	307	−3
	.0142		.000213	4.9	5.6	5.4	6.6	4.7	5.4	335	288	302	+14
	.0154		.000231	5.9	5.2	7.1	3.6	5.0	5.4	335	288	296	+8
	.0204		.000306	2.9	2.8	2.6	2.6	2.3	2.6	310	274	272	−2
350	.0204	.020	.000408	2.4	2.6	3.0	1.6	2.4	2.4	281	242	239	−3
		.015	.000306	4.7	5.0	4.8	7.4	6.6	5.7	308	264	272	+8
		.010	.000204	23.2	-----	20.9	22.2	19.5	21.4	351	303	305	+2
		.005	.000102	40.1	-----	47.6	38.9	29.0	38.9	373	321	337	+16
400	.0115	.020	.000230	3.5	3.5	4.4	4.9	4.1	4.1	341	292	296	+4
		.015	.000162	17.7	-----	13.1	10.0	8.4	12.3	380	327	318	−9
		.010	.000115	29.3	-----	26.9	24.9	29.2	27.6	413	354	333	−20
		.005	.000058	39.2	40.9	33.5	31.0	36.7	36.3	424	362	351	−11
												Average within ± 6 per cent.	

[1] Tests made with steel E97 on test forging No. 40. Composition and treatment of the tools given in Table 2. Tool form shown in Figure 5, B; composition and properties of test forging given in Table 3.

Equation (2) indicates that the cutting speed is a function of the area of cut and affected equally by changes in the depth and feed. This is at variance with the results of Ripper and Burley [11] for shallow cuts and those of Taylor and his associates [12] for rough turning. Ripper and Burley found that "if the area of cut is kept constant a higher associated [13] cutting speed is obtainable when the cut is deep and the feed fine than when the cut is shallow and the feed coarse." They expressed the relations between cutting speed, feed, and depth of cut by the following equation

$$V=\frac{K_1}{F^{2/3}}-(K_2-K_3F)D \qquad (5)$$

in which, K_1 K_2, and K_3 are constants.

[11] See footnote 3, p. 831.

[12] See footnote 2, p. 830.

[13] Cutting speed giving a definite tool life.

It is probable that the cutting speed is not affected equally by changes in the feed and depth of cut, but it is also probable that the differences between the true laws of cutting, and the results obtained on the assumption that the cutting speed is a function of the area of

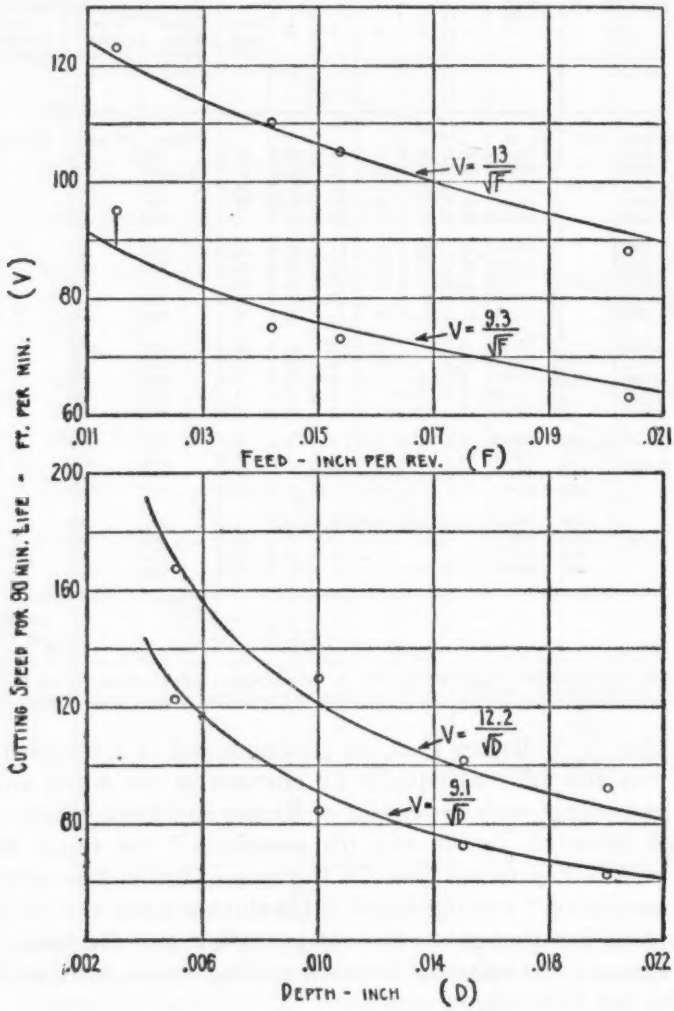

FIGURE 9.—*Effect of feed and depth of cut on the cutting speed of 1.3 per cent C steel tools when taking shallow cuts at fine feeds*

All tests were made dry with steel C 22 (Table 2) on forging No. 41 (Table 3).

cut, will be small in the case of the shallow cuts and fine feeds here investigated.

The experiments made in this investigation using different feeds and depths of cut were not carried out with a view to establishing the laws of cutting. They were made solely to permit a more general

interpretation of the results of tests designed to throw light upon metallurgical variables, such as the composition and heat treatment of the tools. From this standpoint it is immaterial whether one or another form of equation is employed so long as a reasonably close concordance is obtained between the experimental results and the calculated values. In this respect equation (2) seems adequate for present purposes and was used in the extrapolation of experimental data as required in this investigation.

2. FOR CARBON STEEL TOOLS

The effect of feed and depth of cut on the cutting speeds of carbon steel tools is shown in Figures 9 and 10. In this case the relations

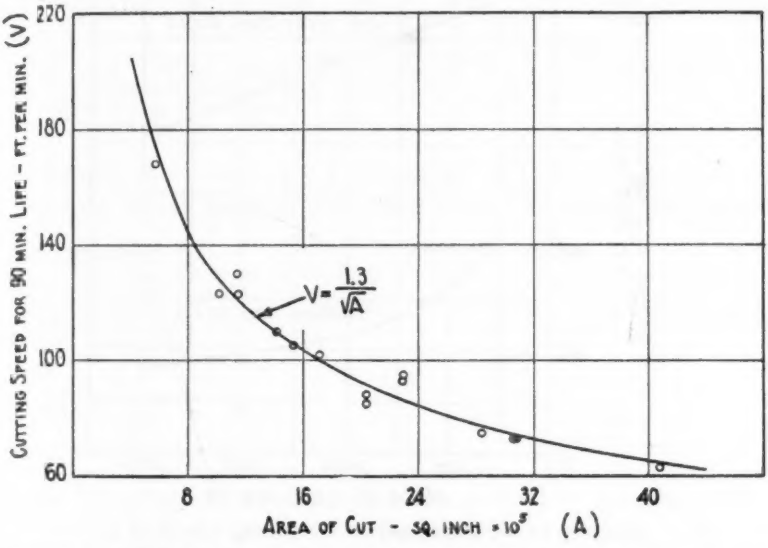

FIGURE 10.—*Effect of area of cut on the cutting speed of 1.3 per cent C steel tools when taking shallow cuts at fine feeds*

All tests were made dry with steel C 22 (Table 2) on forging No. 41 (Table 3).

may be represented approximately by the equation

$$V = \frac{K}{DF} = \frac{K}{A} \tag{6}$$

With the tools and the test forgings used in the experiments and the selected tool life of 90 minutes, equation (6) becomes

$$V = \frac{1.3}{A} \tag{7}$$

where V is expressed in feet per minute and A in square inches.

Under the range of cutting conditions investigated, the cutting speeds for high-speed steel tools were much higher than those for carbon steel tools, but the differences tended to diminish as the areas of cut were decreased. With sufficiently shallow cuts and fine feeds or with adequate cooling it may be possible for carbon steel tools to have higher cutting speeds than high-speed steel tools, as has been reported by some investigators.[14] This is shown graphically in Figure 11, where the cutting speed-area of cut curve for high-speed steel tools is a straight line and that for carbon steel tools rises very rapidly for cuts less than about 0.0001 square inch. The two curves

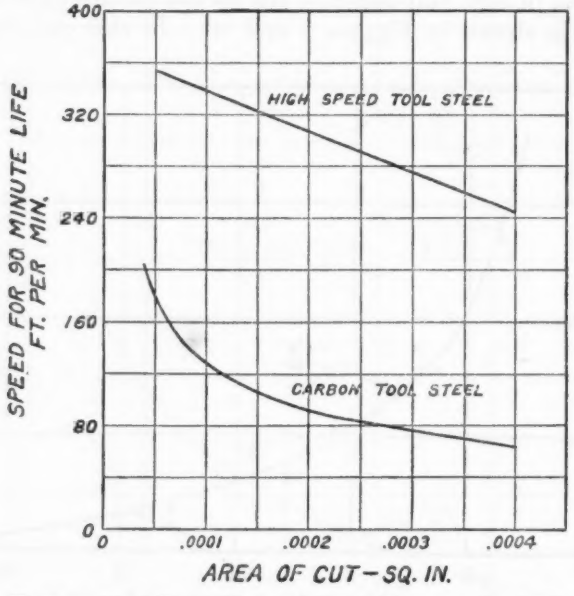

FIGURE 11.—*Comparison of the cutting speeds of 1.3 per cent C and the high-speed steel tools with different areas of cut*

Based on data given in Figures 8, 9, and 10.

may cross with sufficiently small areas of cut or if the tools are working at low temperatures through the use of cutting liquids.

VII. VARIATIONS IN TOOL FORM

1. SHAPE OF THE NOSE OF THE TOOL

Tests were made with tools of different forms and angles with the principal object of determining whether successful application of the described method of test was dependent upon having a broad-nose tool.

[14] See Table 1, p. 832.

Comparisons were first made of the performance of the broad-nose tools, illustrated in Figure 5, *B*, with tools of the forms and dimensions shown in Figures 12, *A* and *B*. Both of the tools illustrated in Figure 12 were similar to tools studied by the Lathe Tools Research Committee [15] except for size, a slight increase in the front and side clearance angles, and in the plan angle of the tool in Figure 12, *A*.

TABLE 7.—*Performance of tools of different forms when taking shallow cuts and fine feeds* [1]

Tool form	Tool life (minutes)										Cutting speed for 90-minute life [2]
	1	2	3	4	5	6	7	8	9	Average	
											Ft./min.
Broad nose (fig. 5, *B*)	17.2	------	27.6	21.8	16.2	11.8	20.0	21.9	24.7	20.1	327
65° plan angle (fig. 12, *A*)	43.0	28.7	40.0	22.4	44.0	20.7	37.5	28.4	------	33.1	344
Pointed tool (fig. 12, *B*)	0	0	0	[3] 6.7	------	------	------	------	------	------	------

[1] Composition and treatment of tool steel E97 given in Table 2. Composition and properties of test forging No. 41 given in Table 3. All tests made at 380 ft./min. cutting speed, 0.0115 in./rev. feed, and 0.010 inch depth except as otherwise noted.
[2] Computed by equation (1) of the text.
[3] This test made at 250 ft./min. cutting speed.

The results of the tests are summarized in Table 7 and show that the tool with a plan angle of 65° had a longer life (and higher cutting

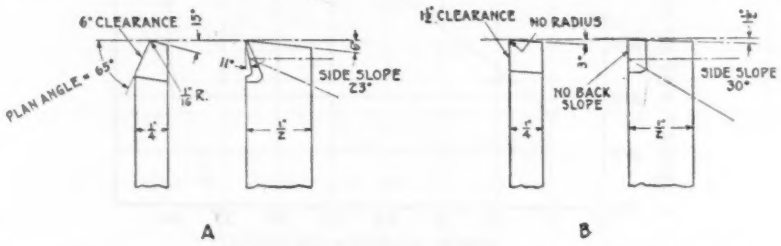

FIGURE 12.—*Tools of special form used in some of the lathe tests under shallow cuts and fine feeds*

speed) than the broad-nose tool illustrated in Figure 5, *B*. The sharp pointed tool (fig. 12, *B*) failed immediately under the conditions of test which permitted the other two tools to cut for 20 to 35 minutes, but with a reduction in the cutting speed from 380 to 250 feet per minute the sharp pointed tools gave evidence of a measurable length of life.

The finish produced on the work appeared to be somewhat smoother and more highly polished with the broad-nose tools (fig. 5, *B*) than with the tools having a 65° plan angle (fig. 12, *A*). The latter tools failed abruptly, whereas with the broad-nose tools failure was progressive from leading to trailing edges as has already been described.

[15] Department of Scientific and Industrial Research, Manchester Association of Engineers. Report of the Lathe Tools Research Committee, 1922, His Majesty's Stationery Office, London.

Spiral chips were characteristic of the broad-nose tools, whereas straight chips and chips which were not as deeply colored were produced by the tools having the 65° plan angle.

2. BACK SLOPE AND SIDE SLOPE IN BROAD-NOSE TOOLS

Further evidence that the trailer tool method of test is applicable to a wide range of conditions is found in the results of tests made with broad-nose tools (fig. 5, *B*) having back slopes varying from 5° to 40° and side slopes of 0° and 8°.

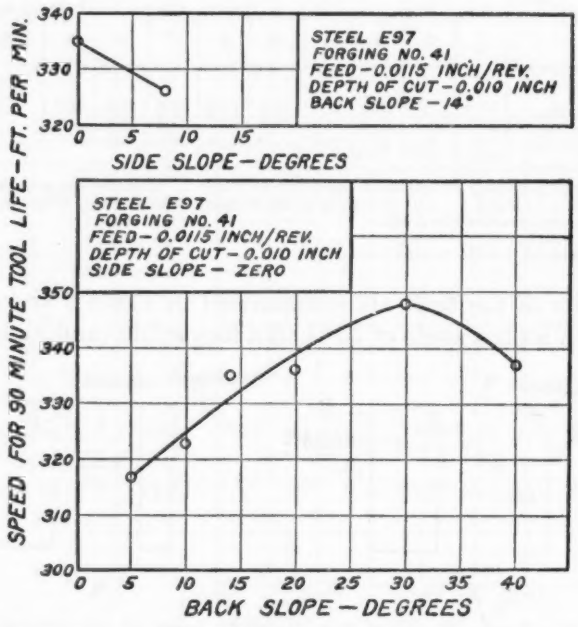

FIGURE 13.—*Effect of change in back slope and in side slope on the cutting speed of the broad-nose tools of Figure 5(B) when made of high-speed steel*

As is shown in Figure 13, the cutting speed of tools with 8° side slope was less than that of tools with 0° side slope, and the best performance of the latter was obtained with about 30° back slope. With increase to 40° or decrease to 5° back slope the cutting speed decreased.

In addition to showing that the broad-nose tools (fig. 5, *B*) had a shorter life but left a more desirable finish on the work than the tools with 65° plan angle and that tool angles affected the performance of the former to an appreciable degree, these tests demonstrate that the successful application of the trailer tool method of test is not dependent upon having tools of a particular form.

VIII. EFFECT OF LARD OIL AND WATER ON CUTTING SPEED OF HIGH-SPEED STEEL TOOLS

Since most industrial machining is done wet, the dry tests, already described, were supplemented by a few tests with water [16] or lard oil [17] as cutting liquids, but instead of making comparisons under one speed, feed, and depth of cut, tests were carried out at different speeds to give durations of cut from about 2 to 50 minutes.

A stream of the chosen liquid was thrown on the top surface of the tool through a ¼-inch nozzle at the rate of approximately 0.35 gallons per minute. Alternate wet and dry tests were made to eliminate, as far as practicable, from the results, variations arising from differences in the machining properties from point to point in the test forgings.

The results of the tests are summarized in Figure 14, and show that there was a gain in the cutting speed (or tool life) from the use of

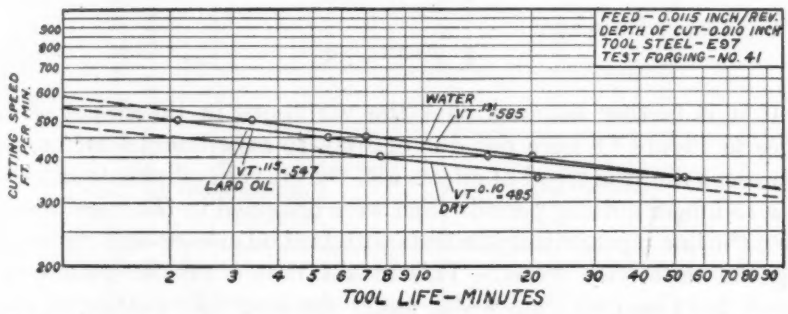

FIGURE 14.—*Relations between the tool life and the cutting speed of high-speed steel tools when cutting wet and dry*

See text for discussion.

either water or the lard oil. The increase was slightly greater with water than with the lard oil in tests of short duration (made with the highest cutting speeds) but equal in the tests in which tool failure occurred in about 50 minutes.

In other words, the slopes of the straight lines representing the relations between cutting speed and tool life in the logarithmic plotting used in Figure 14 were not the same for the wet and dry tests. This may be significant although it should be noted that the differences are not much greater than the scatter of points which can ordinarily be expected with the methods of test employed.

In the tests of short duration the operating temperatures of the tools are known to have been higher than in the tests of long dura-

[16] One and one-half per cent by weight of washing soda was added to the water to minimize corrosion of the machine tool equipment.

[17] The lard oil used was purchased under United States Government master specification No. 2d for Lubricants and Liquid Fuels. Bur. Mines Tech. Paper 323B, United States Department of Commerce, 1927.

tion, and the gains from water, which is a more effective coolant than oils, would be expected to be greater than the gains from the lard oil. With decrease in the cutting speed, the frictional temperatures decreased. There was less need for cooling, and it is not unreasonable to find equal gains from the two liquids.

If it is assumed that the temperatures of the working portions of the tools at given speeds, feeds, and depths of cut decreased in order from the dry tests to tests with the lard oil and water, then it may be said that the slopes of the lines representing the experimental results in Figure 14 increase with decrease in the operating temperatures. The three conditions may then be represented in terms of equation (1), as follows:

For dry tests

$$V T^{0.100} = 485 \tag{8}$$

For tests with lard oil

$$V T^{0.115} = 547 \tag{9}$$

For tests with water

$$V T^{0.131} = 585 \tag{10}$$

If it is further assumed that the variations in the slopes of the lines in Figure 14 were not due entirely to experimental errors, but represent the true trend of effects and that it is justifiable to extrapolate to longer cutting periods than were obtained in the experiments, then the line representing the tests with lard oil crosses that representing the tests with water. This means that a greater gain would result from lard oil than water under the long-time cutting of commercial practice.

These features are of interest, but before they can be accepted without reservations further work should be done, and, as pointed out in a recent report of the American Society of Mechanical Engineers Special Research Committee on Cutting of Metals,[18] much more must be known of the true action of cutting liquids.

Possibly the greatest benefit obtained with the liquids was the better finish produced and not the increase in tool life. In general, dry turning gave a highly polished and smooth finish at the start of the cut, but there was a tendency for the surface to become less smooth as the test progressed, resulting in a very poor finish on the work piece just before tool failure. At this time there was also a tendency toward chattering, and very often small, shiny particles became embedded in the work piece. The finish produced when operating with the liquids was not so highly polished at the start of the cut as when dry. However, it appeared to be as smooth, and this smoothness was maintained throughout the whole cutting time.

[18] Progress Report No. 1 on Cooling and Lubrication of Cutting Tools. Subcommittee on Cutting Fluids. Presented at the December, 1928, meeting of the American Society of Mechanical Engineers.

IX. EFFECT OF HEAT TREATMENT OF TOOLS ON CUTTING SPEED

1. HIGH-SPEED STEEL TOOLS

The performance of high-speed steel tools is quite largely dependent upon the heat treatment to which they have been subjected, and the best results are obtained in rough turning when the customary steels containing about 0.7 per cent carbon, 18 per cent tungsten, 4 per

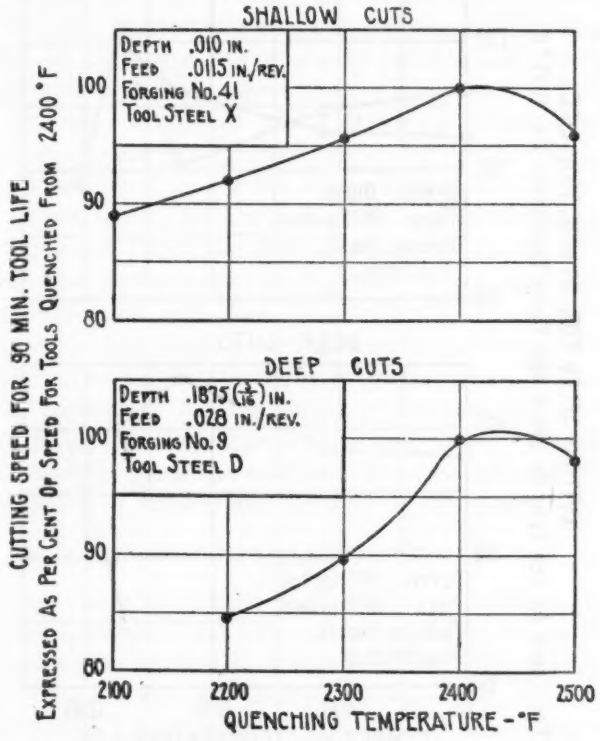

FIGURE 15.—*Effect of quenching temperature on the cutting speed of high-speed steel tools under shallow cuts and under heavy duty*

All tools were tempered at 1,100° F. subsequent to hardening. Compositions of the tools are given in Table 2; properties of the forgings are given in Table 3. All tests were made dry.

cent chromium, and 1.1 per cent vanadium are quenched from 2,400 to 2,450° F. and subsequently tempered at about 1,100° F.[19] This treatment gives close to the maximum tool life, but the tools must be well supported, as they are more brittle than when hardened from lower temperatures.

[19] H. J. French, J. Strauss, and T. G. Digges, Effect of Heat Treatment on Lathe Tool Performance and Some Other Properties of High-Speed Steels, Trans. Am. Soc. Steel Treating, 4, p. 353; 1923.

Tempering at 1,050° to 1,100° F., subsequent to hardening from 2,400° F., may improve the tool life slightly, but a more important effect is improved toughness.

The effect of variations in the hardening temperature upon the life of roughing tools is shown in the lower half of Figure 15, in which the cutting speeds giving 90 minutes tool life are expressed as the

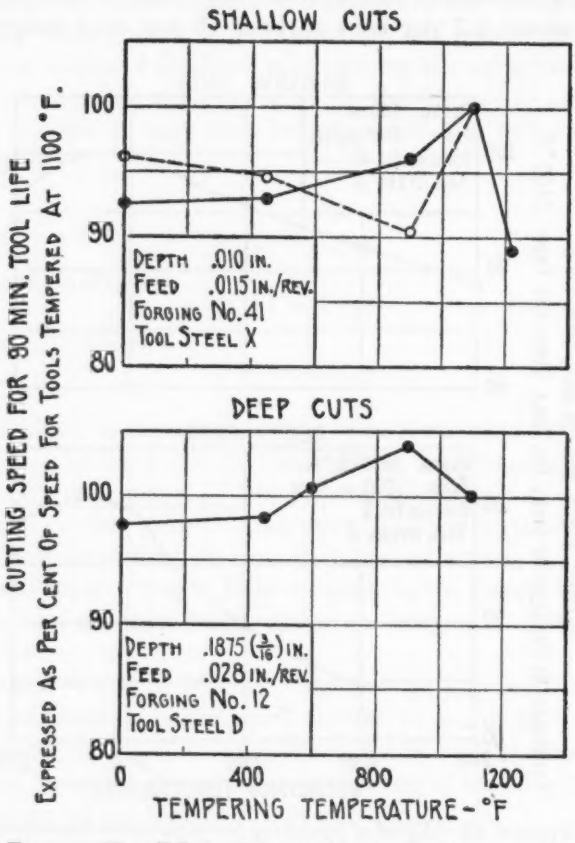

FIGURE 16.—*Effect of tempering temperature on the cutting speed of high-speed steel tools under shallow cuts and under heavy duty*

All tools were first oil quenched from 2,400° F. Compositions of the tools are given in Table 2; properties of the forgings are given in Table 3. All tests were made dry.

percentage of the cutting speed of tools quenched from 2,400° F. Figure 15 shows that the hardening treatments which gave the best results for heavy duty also gave the best results with shallow cuts and fine feeds. However, the percentage differences in the tool performance were somewhat smaller in the case of the shallow cuts than for heavy duty.

The effects of variation in tempering temperature on tool life for both deep and shallow cuts are illustrated in Figure 16 and show that tempering at 1,100° F. tended to improve the tool performance, particularly for shallow cuts and fine feeds. This can probably be explained by the conversion to martensite of the greater part of the austenite retained upon quenching. Under shallow cuts and fine feeds the operating temperatures are closer to atmospheric than under conditions of rough turning where the temperatures are often close to "red heat." With shallow cuts the differences in hardness between the fully martensitic steels and those containing appreciable proportions of austenite are probably maintained throughout the life of the tools and may affect their performance. Differences in hardness probably disappear under the high temperatures reached in rough turning, due to a natural "softening" of all steels with large increases in temperature or to the automatic conversion of the austenite to martensite by the heat generated in the test, or both.

In the foregoing experiments relative to the effects of heat treatment upon the performance of the customary high tungsten-low vanadium high-speed tool steel, the trailer tool method of test for shallow cuts and fine feeds gave results similar to those obtained in the breakdown, or Taylor, tests for rough turning. With some compositions of high-speed steel, notably in the case of that containing nickel, the rough turning experiments and those with shallow cuts did not necessarily place the steels in the same order of performance as will be shown in subsequent sections of this report.

2. 1.3 PER CENT CARBON STEEL TOOLS

Tests were made of carbon steel tools, containing 1.3 per cent carbon, when quenched and tempered at different temperatures, and the results are summarized in Table 8. The cutting speed was not affected to any measurable degree by variation in the hardening temperature from 1,425° to 1,650° F., nor did subsequent tempering at temperatures up to 375° F. change the performance of the untempered tools. The toughness of the tools probably varied considerably under these different heat treatments, but this is not so important with the shallow cuts and fine feeds used in the experiments as with the deep cuts and coarse feeds encountered in rough turning with high-speed steels.

X. PERFORMANCE COMPARISONS OF DIFFERENT CARBON AND LOW-ALLOY TOOL STEELS UNDER SHALLOW CUTS

Tests were made under shallow cuts and fine feeds of carbon steel tools containing from about 0.75 to 1.3 per cent carbon and of a low tungsten "finishing tool steel" and a so-called nondeforming tool steel containing about 1¼ per cent manganese and small proportions

of chromium and tungsten. The object of these tests was to compare the performance of the different compositions when subjected to heat treatments substantially the same as those recommended by the respective manufacturers for general purposes.

TABLE 8.—*Effect of heat treatment on the performance of 1.3 per cent C steel tools* [1]

Hardening temperature (° F.) [2]	Tempering temperature [3]	Cutting speed	Average tool life [4]	Cutting speed giving 90-minute tool life
	° F.	*Ft./min.*	*Minutes*	
1,425		163	20.4	
		161	3.2	
		160	(90)	160
1,425	250	163	1.9	
		160	1.4	
		160	73.7	
		160	(90)	160
1,425	375	163	47.8	
		160	(90)	160
1,425	250	165	38.0	
		163	(90)	
		160	(90)	163
1,525	250	168	0.8	
		165	1.1	
		163	(90)	163
1,650	250	170	3.6	
		165	1.8	
		163	(90)	163

[1] Tests made with steel C22 (Table 2) at 0.0115 in./rev. feed and 0.005 inch depth of cut on forging No. 41 (Table 3).
[2] All tools normalized by heating 45 minutes at 1,675° F. and cooling in still air; held 10 minutes at specified hardening temperature and quenched in water.
[3] Tempered for one hour at specified temperatures.
[4] Bracketed values indicate that the tools did not fail in the designated time.

The results of the tests are summarized in Table 9 and show that the cutting speeds were nearly the same for all of the steels. The tungsten tool steel (V, Table 9) gave somewhat better performance than the manganese steel (U, Table 9), but the differences between the latter and the carbon tool steels were probably within the limits of reproducibility of the results.

The reason why the six steels tested showed comparable performance is probably to be found in the nature of the test. So long as the cutting conditions are such that the operating temperatures do not exceed certain values, which are not known at present, the tools continue to cut for long periods. With small increases in the cutting speed, or other variables, such as feed or depth of cut, this limiting temperature of operation is exceeded and the tools quickly fail. In other words, the test as carried out indicates the relative limits in the temperatures of operation under which the tools will stand up. Tungsten is one of the metals known to improve the resistance to "softening" of steels at high temperatures and has probably been responsible for the slight superiority in the cutting speed of steel V,

Table 9. On the other hand, the ability of steels to resist "softening" with temperature increase is probably not affected appreciably by carbon variations between 0.75 and 1.3 per cent, and the different carbon steels all showed comparable cutting speeds.

TABLE 9.—*Summary of tests with carbon and low alloy tool steels* [1]

Steel	Chemical composition (per cent)				Cutting speed	Feed	Depth of cut	Tool life [2]	Speed for 90-minute life
	C	Mn	Cr	W					
					Ft./min.	*In./rev.*	*Inch*	*Min.*	*Ft./min.*
V	1.34		0.14	2.74	170	0.0115	0.005	4.7	
					168			.6	
					165			(90)	165
U [3]	1.00	1.20	.50	.50	170	.0115	.005	2.3	
					165			3.2	
					163			20.4	
					160			12.7	
					160			1.8	
					158			(90)	158
C14	.76				165	.0115	.005	24.1	
					163			1.0	
					160			(90)	
					150			(90)	160
12A	.89				165	.0115	.005	12.9	
					163			(90)	
					160			(90)	
					150			(90)	163
C2	1.09				165	.0115	.005	.5	
					163			2.5	
					160			(90)	160
C22	1.29				170	.0115	.005	1.5	
					165			3.2	
					163			(90)	163

[1] For compositions and heat treatments in detail see Table 2; tests made on forging No. 41, with composition and properties given in Table 3, tool form shown in Figure 5 *B*.
[2] Bracketed values indicate that the tools did not fail in the designated time.
[3] Type composition, purchased under trade name.

There were no detectable differences in the surfaces produced on the work piece by the different carbon and low-alloy steel tools.

XI. HIGH SPEED STEEL TOOLS OF DIFFERENT COMPOSITIONS USED UNDER SHALLOW AND DEEP CUTS

1. PREPARATION OF THE STEELS AND TOOLS

The chemical composition of high-speed steel tools for rough turning was studied by Taylor and his associates [20] and has since been made the subject of many other experiments.[21] In fact, it is probably safe

[20] See footnote 2, p. 830.

[21] Many papers on this subject will be found in the bibliography of High-Speed Tool Steels, Trans. Am. Soc. Steel Treat., **3**, p. 47; 1922. Only a few of the more recent references are included here. H. J. French, J. Strauss, Lathe Breakdown Tests of Some Modern High-Speed Steels, Trans. Am. Soc. Steel Treat., **2**, p. 1125; 1923 B. S. Tech. Paper No. 228. W. Oertel and F. Polzguter; Beitrag zur Kenntnis des Einflusses von Kobalt und Vanadin auf die Eigenshaften von Schnellarbeitsstahl. Berichte d. Fach. des Vereins deut. Eisenhuttenleute, **47**, p. 1; July 17, 1924. L. Guillet, Les aciers à outils a coupe rapide renfermant du cobalt, Rev. de Met., **22**, p. 88; 1925. R. Hohage and A. Grutzner Schneidversuche mit Schnellarbeitsstahlen. Stahl u. Eisen, p. 1126; July 9, 1925. H. J. French and T. G. Digges Experiments With Nickel, Tantalum, Cobalt, and Molybdenum in High-Speed Steels, Trans. Am. Soc. Steel Treat. **8**, p. 681; 1925. F. C. A. H. Lantsberry High-Speed Steels, Trans. Am. Soc. Steel Treat. **11**, p. 711; 1927.

to say that continuous efforts have been made during the past 20 years to improve the performance of high-speed tool steels intended for heavy duty. Comparable studies have not been made for the shallow cuts and fine feeds which generally characterize finish turning operations, and, accordingly, high-speed steels of different compositions were tested by the "trailer-tool" method described in this report and the results compared with those obtained under heavy duty. Tests were made of important industrial types of high-speed steel, such as the high tungsten-low vanadium steels, the low tungsten-high vanadium steels, and the cobalt steels. A study was also made of additions of appreciable proportions of nickel, molybdenum, titanium, and tantalum and of the effects of elements which may be classed as impurities, such as phosphorus, sulphur, arsenic, antimony, tin, copper and aluminum.

The chemical compositions of the steels tested are recorded in Table 2, and, as there indicated, the majority were experimental melts, but a few commercial steels were included for comparison.

The high-speed steels were not free from all elements other than those reported in Table 2, but, in general, only small proportions of other elements were present. In one or two cases small amounts of aluminum were added to quiet the metal in the ladle. Small proportions of nickel, cobalt, or molybdenum were probably introduced through the scrap high-speed steel which formed part of the charge in some of the heats, and other elements were probably introduced inadvertently through their presence as impurities in the ferro-alloys employed.

Spectroscopic examination [22] was made of samples from many of the experimental steels and, with the exception of phosphorus, sulphur, and arsenic, which are not very sensitive in arc spectra, the results confirmed those obtained by chemical analysis, as reported in Table 2. In addition to these elements, small proportions of impurities were found, as follows: Copper, aluminum, and molybdenum were found in all the steels examined, but with the exception of the steels to which these metals were intentionally added the proportions were small and considered to be below 0.03 per cent. Small proportions of tin, introduced from the ferrotantalum, were found in the tantalum steels, E44, E45, E16, and E100. Nickel was found in samples E70, E71, E77, E51, and E87. Cobalt was found in steel E51. Nickel, cobalt, and molybdenum were present in steel E51 and, if 100 per cent recovery of these elements from the high-speed steel scrap is assumed, steel E51 contained about 0.35 per cent cobalt, 0.25 per cent nickel, and 0.10 per cent or less of molybdenum.

Steels L and E97 (Table 2), used as the basis of comparisons in the study of impurities, contained traces, estimated at 0.01 to 0.03 per

[22] Examinations made by Dr. W. F. Meggers, chief of the spectroscopy section.

cent, of copper and aluminum, but there was no evidence of antimony or arsenic. The most sensitive tin lines are close to iron lines, and therefore it was difficult to get a positive indication of tin which may likewise be present in traces in these two steels.

In general, only small proportions of impurities were found by spectroscopic analysis, and these should not affect the comparisons to be made, particularly as steels containing different proportions of the added elements are available in most cases to show the trends in the effects produced.

In the study of impurities, the proportions of arsenic, tin, copper, etc., were much higher, in most cases, than the proportions which would ordinarily be encountered in commercial high-speed steels, but it is frequently advantageous to deal with extremes so as to emphasize the effects of important variables. It should also be kept in mind that the phosphorus, sulphur, arsenic, antimony, copper, or tin were not residual but were added to the steels in the ladle and that the effects produced may differ from those observed when the corresponding elements are carried through all stages of manufacture from the ores or introduced into the steels in other ways. Nevertheless, the ladle additions made constitute a logical step in the study of the subject of impurities.

The steels produced experimentally were melted in an indirect arc furnace. The molten steel was generally tapped hot enough to permit its being held in the ladle for a few moments before casting into 55-pound ingots having a top section about 3 by 3 inches and a length of 22 inches. A split iron mold was used in which the ratio of mold weight to ingot weight was about 1.9; in practically all cases hot tops were used and a top discard made of about 25 per cent.

The required amounts of metallic antimony, arsenic, copper, tin, or aluminum were placed in the ladle and the molten steel poured on top. Phosphorus and sulphur were introduced into the steels by ladle additions of ferrophosphorus containing about 25 per cent phosphorus and pyrite (FeS). The titanium and tantalum were added to the metal in the furnace by placing the required amounts of their respective ferro-alloys in sheet-steel containers and pushing these below the surface of the bath about five minutes before tapping. The recovery varied but did not exceed about 50 per cent of the titanium added as carbon-free ferrotitanium of the composition shown in Table 10.

With the exception of steel E51, the steels containing titanium also contained aluminum which was introduced by the ferro-alloys used. It was largely on this account that two steels, E78 and E98, (Table 2) were made with aluminum additions. Any marked effects produced by titanium could then be determined by comparison of the steels

containing both titanium and aluminum with those containing only aluminum.

TABLE 10.—*Ferro-alloys used in making some of the special high-speed tool steels*

Ferro-alloy	Chemical composition [1] (per cent)									
	C	Mn	Si	Al	Ti	Ta	Cb	Mo	W	Sn
Carbon-free ferrotitanium			2.0	5.9	25.5					
Ferrotantalum	0.21	2.54	3.4			72.2	8.9			−0.1
Ferromolybdenum [2]	.23							59.6		
Ferrotungsten containing molybdenum [3]	.07		.14					4.0	85.1	

[1] As reported by the manufacturer.
[2] P=0.057 per cent; S=0.19 per cent.
[3] Made from California Scheelite ore.

In one case about 97 per cent of the tantalum was recovered when using low-carbon ferrotantalum, but, in general, the recovery was appreciably less varying from about 60 to 80 per cent. As will be noted from Table 10, the ferrotantalum used contained roughly 1 part of columbium for every 8 parts of tantalum. While the steels made will be referred to as tantalum steels, it is to be understood that they also contain columbium. This element, if recovered in the same proportions as tantalum, is present in the steels in amounts equal to about one-ninth of the total percentages given in Table 2.

Molybdenum additions were made in the furnace with the original charge by means of ferromolybdenum of the compositions given in Table 10. However, in two cases—those of heats E107 and E109 (Table 2)—the molybdenum was introduced as an impurity in the ferrotungsten (Table 10). Cobalt was added in shot or cube form in the furnace with the original charge, while nickel was added as shot or electrolytic nickel in the furnace or in the ladle.

After casting the ingots were allowed to become cold and were then annealed. Surface imperfections were removed on a shaper or surface grinder. Steels with heat numbers between E14 and E51, inclusive, (Table 2) were forged with a steam drop hammer to ¾ by 1¼ inch bars; all other steels were forged to 2 by 2 inch bars under a press and then rolled into 1½ by 1½ inch bars. Forging and rolling temperatures were kept between about 2,150° and 1,800° F. Subsequent to forging or rolling the bars were again annealed by heating two to three hours at 1,600° to 1,650° F. and slowly cooling in the furnace.

Test tools about 5 inches long, with a cross section of ½ by ¼ inch, were machined from the rolled or forged bars, and care was taken in grinding the nose to have the top surface of the finished tool comprised of metal adjacent to the surfaces of the hot finished bars.

The tools were preheated for 20 minutes at around 1,600° F., introduced into the high-temperature furnace and kept there one and one-half minutes, and then quenched in a thin oil. They were subsequently tempered 30 to 45 minutes at temperatures given in

Table 2. The results described in Section IX, 1 of this report and earlier work [23] form the basis of selection of the hardening temperatures used which are recorded in Table 2. In most cases these are known to produce close to the best performance of which the several steels are capable. This does not apply to the steels containing tantalum nor to the commercial steels containing the highest proportions of cobalt, which in individual cases were treated by or according to the recommendations of the manufacturer.

2. HOT WORKING AND MACHINING PROPERTIES

An adequate idea of the working and machining characteristics of the steels listed in Table 2 can probably be obtained only under conditions approaching those of commercial production, but certain definite effects were observed in the working and machining of the experimental melts which deserve mention at this time.

Difficulties were encountered in forging two of the molybdenum steels, E31 and E29. (Table 2.) In both heats the ingots cracked badly, and only small proportions were secured in final bar form. The tungsten-molybdenum steel (E31) was, perhaps, the worst in this respect, as the ingot split under the first few light blows of the hammer. Possibly, modifications in the forging practice employed would have been productive of better results, but it appeared that these molybdenum steels were more sensitive to working conditions than the ordinary types of high-speed steel.

So-called "sweating out" of the molybdenum visible by the thick, bluish smoke arising from the steel was observed only during forging (not in heat treatment), but examination of the forged bars of steel E29 indicated negligible losses of molybdenum. Quite probably the smoke observed in forging was the volatilization of the molybdenum oxide already forming part of the scale.

One of the forged and annealed bars was first pickled in an ammoniacal citrate solution to loosen the scale which was then carefully brushed or chipped from the underlying metal. Six successive cuts, each 0.003 inch deep, were then taken beneath the cleaned surface and each of the six samples analyzed for molybdenum. Table 11 indicates negligible losses of molybdenum in the unoxidized metal unless the losses were concentrated in very shallow outer layers. However, this seems improbable since, as pointed out by Bain,[24] molybdenum volatilizes very slowly, even in vacuuo, and diffuses slowly in iron alloys, whereas the oxide of molybdenum is quite volatile. Rapid diffusion and rapid volatilization would both be

[23] See footnote 19, p. 855.

[24] E. C. Bain, Discussion of Paper, referred to in footnote 21, p. 865, by H. J. French and T. G. Digges on Experiments with Nickel Tantalum, Cobalt, and Molybdenum in High-Speed Steels, Trans. Am. Soc. Steel Treating, 8, p. 6; 1925.

necessary for appreciable losses of metallic molybdenum at the unoxidized surfaces of the steel.

The steel containing 0.78 per cent aluminum did not have as good hot-working properties as steels without appreciable proportions of this element, as was shown by bad corner cracks produced in rolling. (Fig. 17.)

One of the steels containing titanium (E96) showed a high degree of hot shortness in rolling although it seemed to forge in a satisfactory manner. This was probably not due either to the aluminum (0.08 per cent) or to high carbon (1.24 per cent), since a steel with equal carbon (E101) and steels with higher proportions of aluminum (0.38 per cent aluminum in steel E101 and 0.30 per cent aluminum in steel E87) had more satisfactory working properties. The splitting of the forged bar in rolling as is shown in Figure 17 may have been due to segregation. In this connection it should be noted that in this steel the recovery of titanium was only about 15 per cent of that added to the molten metal.

TABLE 11.—*Molybdenum found in successive layers beneath the surface of forged bars of steel E29* [1]

Location of sample with respect to pickled and brushed surface	Molybdenum
	Per cent
Entire cross section of bar	7.18
0 to 0.003 inch below surface	7.06
0.003 to 0.006 inch below surface	7.14
0.006 to 0.009 inch below surface	7.19
0.009 to 0.012 inch below surface	7.15
0.012 to 0.015 inch below surface	7.16
0.015 to 0.018 inch below surface	7.16

[1] Chemical composition given in Table 2.

In general, the difficulties in hot-working the different steels were more pronounced in rolling than in forging or pressing. The steels containing 1.7 per cent antimony or 1.8 per cent tin showed a high degree of hot-shortness and could not be forged or rolled. (See Fig. 18.) The ingot of steel E48 containing 1.2 per cent tin "smoked" in forging like the high molybdenum steels.

None of the other steels gave appreciable difficulties in forging, but several showed surface cracks, mostly at the corners, on rolling. Among these were the steels containing 0.4 per cent antimony, the steels with around 0.8 per cent or more of copper, the steel containing 0.8 per cent arsenic, and the steel containing 1.4 per cent carbon and 1.10 per cent tantalum.

All of the high-speed steels referred to in Table 2 could themselves be readily machined when in the annealed condition except the steel containing 1.8 per cent copper and the three steels containing about 3¾ per cent nickel and 0.6 to 0.7 per cent carbon. The steel with

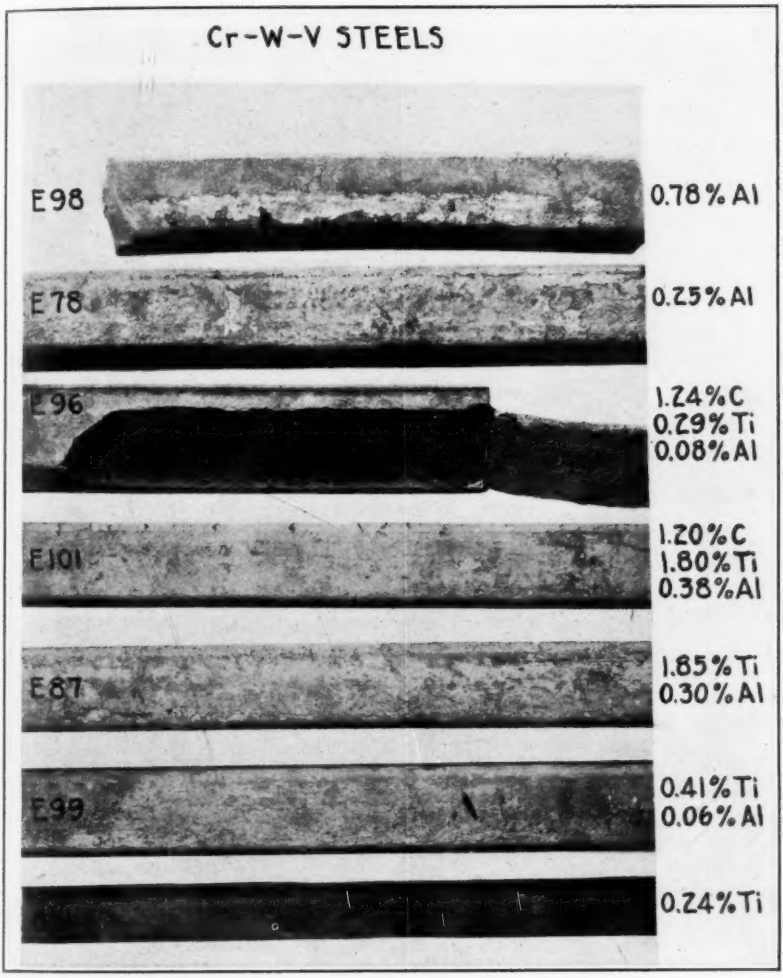

FIGURE 17.—*Appearance of some of the rolled or forged high-speed steel bars containing titanium and aluminum*

See Table 2 for detailed chemical composition.

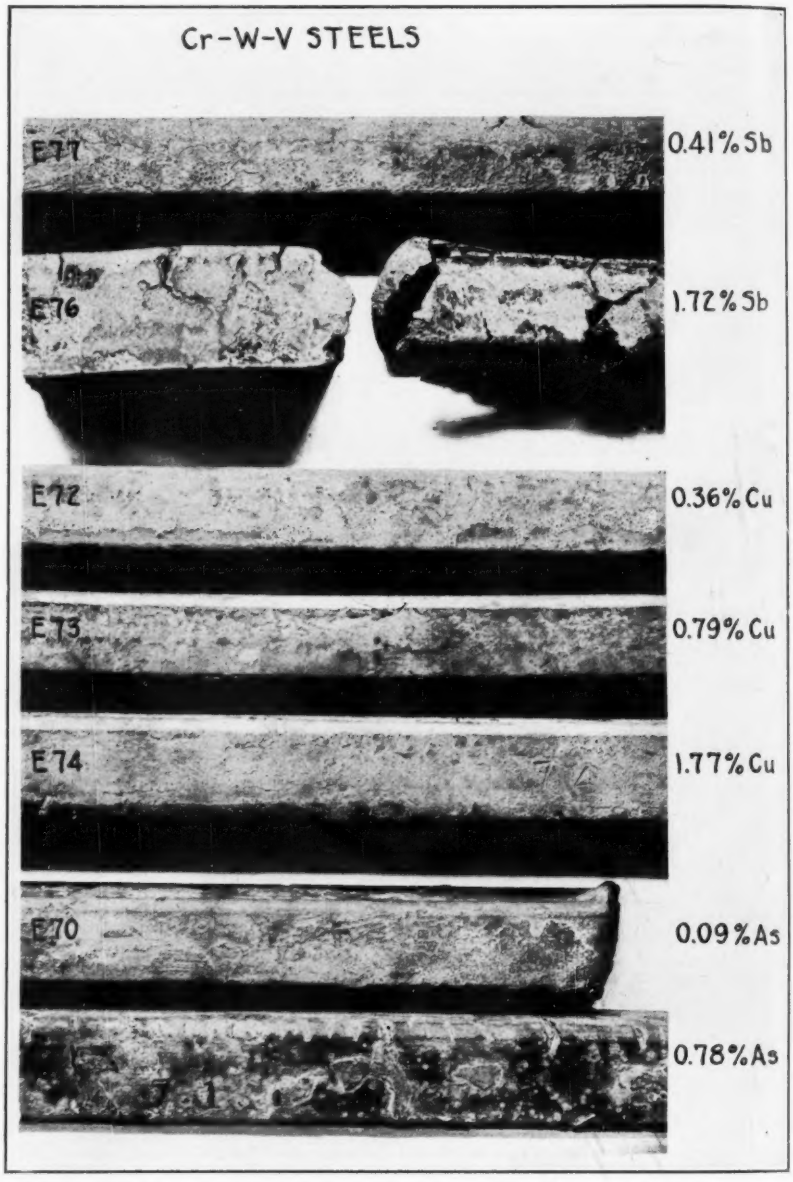

FIGURE 18.—*Appearance of the rolled high-speed steel bars containing arsenic, antimony, or copper*

See Table 2 for detailed chemical composition.

copper (E74) was machined with difficulty, but it was impossible to machine two of the nickel steels, E22 and E14, either in the cast or forged conditions even after prolonged annealing. Steel E130 was machined with difficulty, but with comparable proportions of nickel and lowered carbon content the machining properties were greatly improved. Steel E41 containing about 0.5 per cent carbon and 3½ per cent nickel, while not "soft," could be machined without great difficulty after annealing.

3. GENERAL COMMENTS ON LATHE TESTS

The steels referred to in Table 2 and the lathe-tool tests to be discussed were made at intervals over a long period of time on different test forgings, so that a direct comparison of all the tools is not practicable. This does not prevent determination of the effects of the added metals considered, since each set of tests was considered to be complete in itself and included one or more of the plain chromium-tungsten-vanadium high-speed steels as the basis for comparisons.

All tests were made at selected speeds, feeds, and depths of cut and the tool life determined. From 6 to 12 tools of each steel were tested for each of the selected cutting conditions. However, instead of reporting the average tool life comparisons are made of the cutting speed permitting a tool life of 90 minutes. This was obtained from the average tool life by means of equation (1) with $n=\frac{1}{10}$ for tests made under shallow cuts and fine feeds ("trailer-tool" tests) and with $n=\frac{1}{7}$ for tests made with heavy cuts and coarse feeds (rough turning).[25]

The chromium-tungsten-vanadium steels used as the basis of comparisons in a majority of cases were experimental melts made in the same manner as the steels containing additions of the special elements. However, in some cases commercial high-speed steels were substituted for the experimental steels, so that the performance of the different lathe tools might be viewed in the light of commercial products. The results recorded in Table 12 show that the experimental steels gave comparable performance to the commercial steels of like composition which were selected for comparisons under either shallow cuts and fine feeds or deep cuts and coarse feeds.

4. STEELS WITH MOLYBDENUM

Many of the cobalt high-speed steels contain from 0.5 to 1 per cent of molybdenum, but ferrotungsten containing appreciable proportions of molybdenum has not always been considered to be desirable by American steel manufacturers.[26]

[25] The basis of the selected values for the exponent n in equation (1) is discussed in Section V of this report and in the reference of footnote 1, p. 830.

[26] Private communications.

TABLE 12.—*Comparisons of commercial and experimental high-speed tool steels in lathe tests*

SHALLOW CUTS AND FINE FEEDS

Steel No.[1]	Type of steel	Cutting conditions				Number of tools tested	Average tool life	Remarks
		Speed	Feed	Depth	Forging No.[2]			
		Ft./min.	*In./rev.*	*Inch*			*Minutes*	
L	Low W—high V	400	0.0154	0.005	40	10	47.1	Commercial steel.
E97	Low W—high V	400	.0154	.005	40	10	48.8	Experimental melt.
A	Low W—cobalt	380	.0115	.010	41	6	20.7	Commercial steel.
E15	Low W—cobalt	380	.0115	.010	41	6	19.3	Experimental melt.

DEEP CUTS AND COARSE FEEDS

L	High W—low V	85	0.028	0.1875	17	8	7.4	Commercial steel.
E21	High W—low V	85	.028	.1875	17	8	6.3	Experimental melt.
A	Low W—cobalt	100	.028	.1875	42	6	13.8	Commercial steel.
E15	Low W—cobalt	100	.028	.1875	42	6	14.1	Experimental melt.

[1] See Table 2 for chemical compositions of the tools and their heat treatment; tool form given in Figure 5, *B*.
[2] See Table 3 for chemical compositions and properties of the forgings cut.

The four steels containing molybdenum (Table 2) may be said to fall into two classes, the one in which molybdenum was introduced as an impurity in the ferrotungsten, made from California Scheelite ores, and the second in which molybdenum was used intentionally as a replacement of part or all of the tungsten.

Steels E109 and E107 were made with the idea of determining whether small amounts of molybdenum produced any appreciable effects upon the tool performance of the customary chromium-tungsten-vanadium high-speed steels. In steels E31 and E29 part or all of the tungsten was replaced by molybdenum in the approximate ratio of 1 part molybdenum for each 2½ parts of tungsten. This ratio represents approximately equivalent effects as determined in lathe-tool tests by Arnold and Ibbotson.[27]

While not strictly accurate, all four of the steels with molybdenum may be considered to be modifications of the customary high tungsten-low vanadium high-speed steel in which 1 part of molybdenum has replaced approximately 2½ parts of tungsten, and it is on this basis that the results of the lathe tests are summarized in Figure 19.

It would appear from Figure 19 that molybdenum may be substituted for part or all of the tungsten without radically changing the lathe-tool performance under shallow cuts and fine feeds or under heavy duty. If the results in Figure 19 show any definite trends, they are that molybdenum is somewhat disadvantageous from the standpoint of shallow cuts, but may improve the steels for heavy duty.

[27] J. O. Arnold and F. Ibbotson, The Molecular Constituents of High-Speed Tool Steels and Their Correlations with Lathe Efficiencies, J. Iron and Steel Inst., **99**, No. 1, p. 407; 1919.

More definite conclusions can not be drawn, since steels E31 and E29 are, respectively, low in carbon and in vanadium, and the importance of these variations when taking shallow cuts is not known at this time.

The performance of the molybdenum steel, E29 (without tungsten), was somewhat irregular under shallow cuts, as is shown in Table 13. The cutting speed in one set of tests was almost identical with that of the tungsten steel E97 but in another set of tests made with a deeper cut was somewhat lower.

The rough turning tests did not establish superiority or inferiority of the high-speed steel tools containing molybdenum, and in this respect the results in Figure 19 are consistent with those obtained by earlier investigators who, in some cases, found that the steels with molybdenum gave better performance than the tungsten steels,

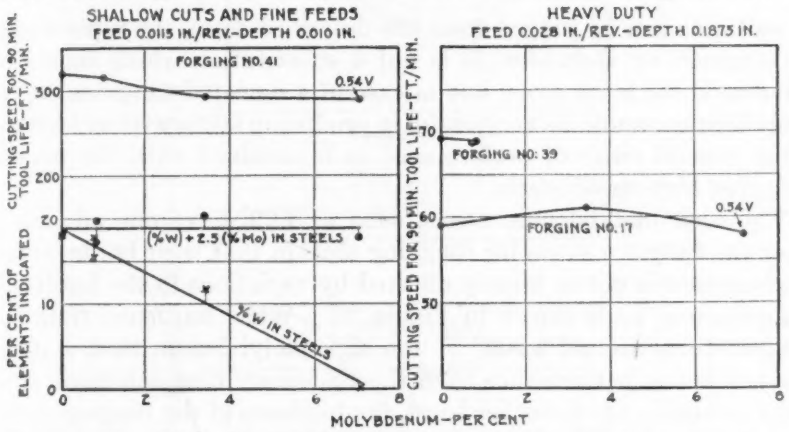

FIGURE 19.—*Effect of molybdenum on the cutting speed of chromium-tungsten-vanadium steel tools when taking shallow cuts and when tested under heavy duty*

The molybdenum in these steels replaced a part or all of the tungsten as indicated graphically on the left side of the chart and as explained in the text. Compositions of the tools and their heat treatment are given in Table 2; properties of the forgings are given in Table 3. All tests were made dry.

while in other cases this order was reversed. Detailed comparisons of the results of some previous investigations are given in Table 14.

TABLE 13.—*Performance comparisons under shallow cuts of Cr–Mo–V and Cr–W–V high-speed steel tools*

Steel No.[1]	Chemical composition (per cent)					Cutting conditions				Average tool life	Cutting speed for 90-minute tool life[2]
	C	Cr	W	V	Mo	Speed	Feed	Depth of cut	Forging No.[1]		
						Ft./min.	*In./rev.*	*Inch*		*Minutes*	*Ft./min.*
E97	0.64	3.41	13.02	1.99	------	380	0.0115	0.010	41	16.4	320
E29	.71	4.74	------	.54	7.07	380	.0115	.010	41	6.0	290
E97	.64	3.41	13.02	1.99	------	400	.0115	.005	41	14.6	333
E29	.71	4.74	------	.54	7.07	400	.0115	.005	41	13.8	332

[1] See Tables 2 and 3, respectively, for details of tool steel treatments and properties of forging No. 41; tool form shown in Figure 5, *B*.

[2] Computed by means of equation (1) of the text with $n=\frac{1}{10}$.

TABLE 14.—*Roughing lathe-tool performance of high-speed steels with and without molybdenum reported by some earlier investigators*

Chemical composition (per cent)					$W+2\frac{1}{2}\times Mo$	Relative tool performance	Metal removed in speed increment tests	Source of data
C	Cr	W	V	Mo				
					Per cent		*Pounds*	
0.79	4.27	23.90	0.69	------	23.90	1.35	--------	Hohage and Grutzner; Stahl u. Eisen, July, p. 1126; 1925.
.79	3.18	12.40	.52	3.98	22.35	1.00	--------	
.63	3.14	18.70	.49	------	18.70	1.02	--------	
.55	2.62	15.93	1.16	------	15.93	--------	110	Arnold and Ibbotson; J. Iron and Steel Inst., **99**, p. 407; 1919.
.76	2.82	12.12	1.28	2.06	17.27	--------	96	
.75	2.79	--------	1.29	5.79	14.47	--------	112	

As far as can be judged from the described tests, the replacement of tungsten by molybdenum is not a substitution which should be advocated for lathe tools, but in case of a depleted tungsten supply molybdenum would be very useful in producing steels with at least the same general order of performance as is obtained with the present tungsten high-speed steels.

The high molybdenum steels, such as E29, have one advantage over the tungsten steels for roughing tools in that their hardness and performance is not so largely affected by variations in the hardening temperatures as is shown in Figure 20. When hardened from low temperatures around 2,200° F. the high molybdenum steel actually showed better performance than the customary tungsten steels similarly treated. On the other hand, the hardness of the tungsten steels containing 1 per cent or less of molybdenum was the same as that of corresponding steels without molybdenum when subjected to the same heat treatments.

Up to the present time it has not been practicable to expect uniformly good performance from high-molybdenum high-speed steel tools, but more extended experience with such steels would probably result in the development of a technique in manufacture and handling which would result in a more satisfactorily uniform performance.

5. STEELS WITH COBALT

Cobalt has been an important element in the so-called tungstenless alloys for high-speed cutting tools, but the steels considered here are the customary chromium-tungsten-vanadium steels modified only by additions of cobalt. In the commercial steels of this type from 2.5 to 5 per cent of cobalt has usually been added, but more recently steels with much higher proportions of cobalt have been placed on the American market. Some of these also contain molybdenum in proportions up to about 1 per cent, but since the results already described showed that 1 per cent or less of molybdenum had no appreciable

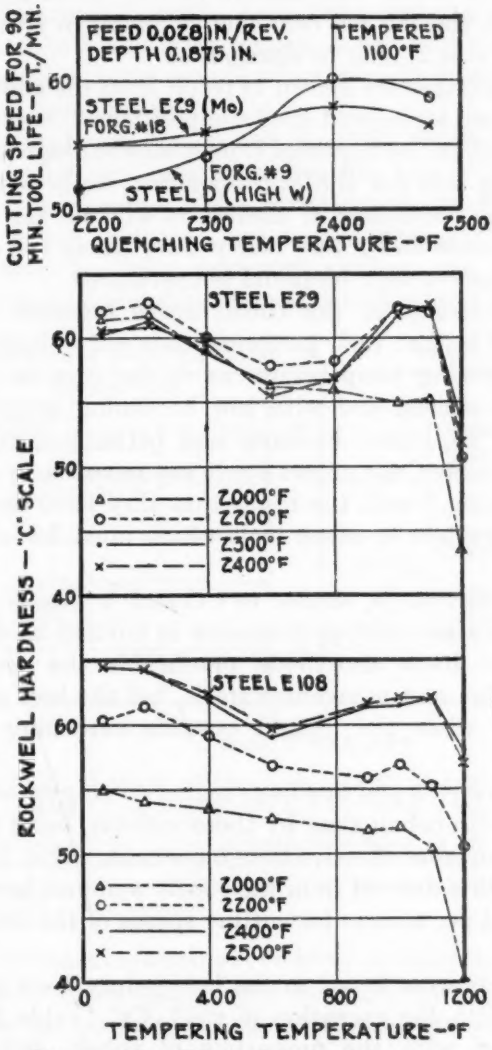

FIGURE 20.—*Effect of heat treatment on the cutting speed and hardness of some of the high-speed steels containing molybdenum*

Composition of the tools and their heat treatments are given in Table 2; properties of the forgings are given in Table 3. All lathe tests were made dry. Quenching temperature shown in the body of the chart. The cutting speed of steel D containing no molybdenum is given for comparison with the molybdenum steel E29.

influence on the cutting speeds of the customary chromium-tungsten-vanadium steels, either with shallow cuts or under heavy duty, the presence of 0.6 and 0.9 per cent molybdenum, in steels CC and Y, repesctively, Table 2, may be disregarded.

Several advantages are known to result from the addition of cobalt to the customary high-speed steel compositions. Steels with around 5 per cent cobalt can be hardened from somewhat higher temperatures than would be safe for the corresponding steels without cobalt,[28] and under such conditions of treatment will, on the average, give better performance under very heavy duty where the deep cuts and coarse feeds produce high frictional temperatures.

Another advantage of the cobalt steels reported by European investigators [29] is that their performance is not so largely dependent upon the hardening temperatures as is the case in corresponding steels without cobalt, and with low hardening temperatures, say, around 2,300° F., higher hardness and better performance can be expected. However, the cobalt steels are reported to acquire a soft skin on hardening,[30] with the result that they have not been widely used in form cutters or other tools which must be heat treated in finished form.

The high-cobalt steels, similar to CC and Y (Table 2), have been reported to give excellent performance in cutting hard metals; it is claimed [31] they have also made practicable the commercial machining of 14 per cent manganese steels, but the best performance is obtained only when the highest possible hardening temperatures are used.

Under shallow cuts and fine feeds higher cutting speeds were shown by the steels with cobalt than by those without, but 8 to 12 per cent of cobalt was no more effective than 5 per cent. (Fig. 21.) Furthermore, the benefits derived from the cobalt were not large, amounting to 10 to 25 feet per minute for cutting speeds of the order of 325 feet per minute.

Similar effects were found in the heavy-duty tests as is shown in Figure 21. With the exception of steel, CC (Table 2) the cutting speed increased with the proportion of cobalt, but the increase between 3.5 and 12 per cent was not nearly as large as that between 0 and 3.5 per cent. With 3.5 per cent cobalt, there was a somewhat larger percentage gain in the heavy-duty tests than in the tests under shallow cuts and fine feeds.

Superior performance of the steel with 3.5 per cent cobalt was probably due to the fact that it was hardened from a temperature

[28] See footnote 19, p. 855. Also F. Repatz, Die Leistung von Schnellstahlmessern und ihre Prüfung. Stahl u. Eisen, **49**, p. 1109; 1926.

[29] L. Guillet, Les aciers à outils a coupe rapide refermant du cobalt. Rev. de Met., **22**, p. 88; 1928.

[30] F. C. A. H. Lantsberry, High-Speed Steels, Trans. Am. Soc. Steel Treating, **11**, p. 711; 1927.

[31] A. S. Martin, Machining Manganese Steel on a Commercial Basis, Iron Trade Rev., **82**, p. 564; 1928.

50 to 75° F. higher than that used in hardening the 8 and 12 per cent cobalt steels and the steel without cobalt. Results reported by Oertel and Polzguter,[32] which have been included in Figure 21, indicate that cobalt additions around 3 per cent do not result in greatly increased cutting speeds when the steels are all hardened from the same temperatures.

There is little doubt that cobalt by itself tends to increase the cutting speed, but the maximum benefits are derived only with modified heat treatments. The results given in Figure 21 show further that cobalt additions are of somewhat greater benefit for heavy duty than for tools used with shallow cuts and fine feeds. But in rough turning nickel steels, such as were used in the described

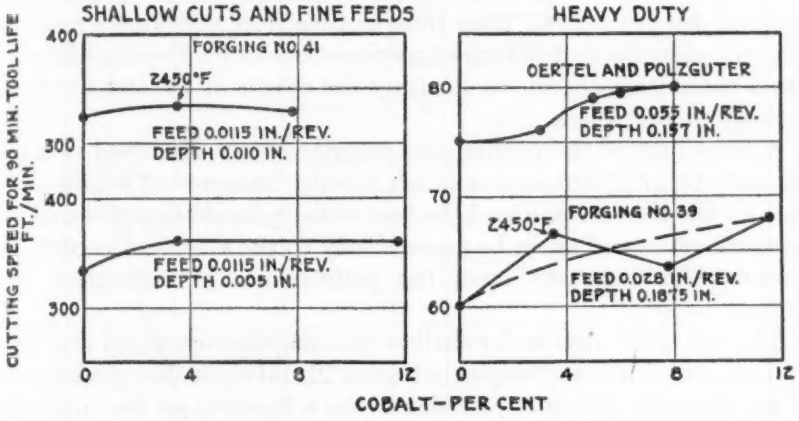

FIGURE 21.—*Effect of cobalt on the cutting speed of high-speed steel tools when taking shallow cuts and under heavy duty*

Compositions of the tools are given in Table 2; properties of the forgings are given in Table 3. Unless otherwise indicated, the tools were oil quenched from 2,375° to 2,400° F. and tempered at 1,050° to 1,100° F. All tests were made dry. The source of the data credited to Oertel and Polzguter is given in footnote 21, p. 859 of the text.

experiments, increase in cobalt above about 5 per cent did not produce improvements commensurate with those resulting from additions of 3.5 to 5 per cent cobalt and high hardening temperatures.

6. STEELS WITH ARSENIC, ANTIMONY, COPPER, OR TIN

As a general rule, little attention is paid by consumers to the presence of copper, tin, arsenic, or antimony in commercial high-speed tool steels, although it is known that all of these elements will be found occasionally, and some of them frequently, in the American products. Some may be introduced from scrap which forms part of the original charge, or, as is sometimes the case with tin and arsenic, small proportions may be present as impurities in the ferro-alloys used in manufac-

[32] See footnote 21, p. 859.

ture. In any case, arsenic, antimony, copper, and tin are generally believed to exert harmful effects upon high-speed tool steels.

According to Sandberg,[33] copper, tin, arsenic, bismuth, and antimony are ordinarily present in small amounts in high-speed steels but have no ill effects unless they are present, individually, in excess of 0.02 per cent. McKenna [34] states that the detrimental effects of tin, copper, and arsenic are not generally realized by the trade, and that small quantities of these impurities are exceedingly harmful. The character of the data upon which these statements are based is not known, and technical literature does not contain information on the magnitude of the effects produced by different proportions of the metals in question or whether they are equally deleterious for all classes of serivce. The need for further information is shown by inquiries which have been received by the bureau from time to time from consumers and producers and by the fact that the American Society for Testing Materials has a committee appointed to study the effects of tin and arsenic in high-speed tool steels.

A large part of the results here described were discussed in a preliminary report,[35] but since a much broader background is now available for the interpretation of the tool tests under shallow cuts and fine feeds reference will again be made briefly to the effects of copper, tin, arsenic, and antimony upon the performance of high-speed steel turning tools.

The results of tests under shallow cuts and fine feeds and also those under heavy duty are grouped in Figure 22 and show that the influence of the different elements considered was a function of the conditions to which the tools were subjected.

With shallow cuts, each of the four elements—copper, tin, arsenic, and antimony—adversely affected the tool performance and in each case the magnitude of the decrease in tool life or the cutting speed became greater as the proportion of the impurity was increased. Copper was the least harmful; next in order came tin, while arsenic and antimony were the most objectionable.

The effects of the several elements upon the performance of roughing tools did not necessarily correspond to those observed with shallow cuts. The arsenic addition lowered the cutting speed, but the addition of 0.4 per cent antimony or 0.5 per cent or less of tin had no measurable effect. Higher proportions of tin lowered the cutting speeds, but the high-speed steels containing copper showed slightly better performance than the corresponding steels without copper.

[33] R. M. Sandberg, Progress in Hardening High-speed Steel, Fuels and Furnaces (F. C. Andresen and Associates, Pittsburgh, Pa.), **6**, No. 1, p. 53; January, 1928.

[34] R. C. McKenna, Practical Information Concerning High-Speed Steel, Am. Machinist, **51**, p. 989; 1919.

[35] H. J. French and T. G. Digges, Effects of Antimony, Arsenic, Copper, and Tin in High-Speed Tool Steel, Trans. Am. Soc. Steel Treat., **13**, p. 919; 1928.

This effect was confirmed in two independent sets of tests as is shown in Figure 22.

The described results seem to justify the conclusions that copper has the least harmful effects of the four metals here considered upon the cutting speeds of high-speed steel turning tools; that small proportions of tin, below about 0.1 per cent, do not seriously affect the cutting speeds; but that arsenic and antimony should be kept out of high-speed tool steels to be used under varied conditions of service.

In general, the presence of small proportions of these different elements is much less important for tools to be used only in rough turning than when shallow cuts are considered. This is, perhaps, to

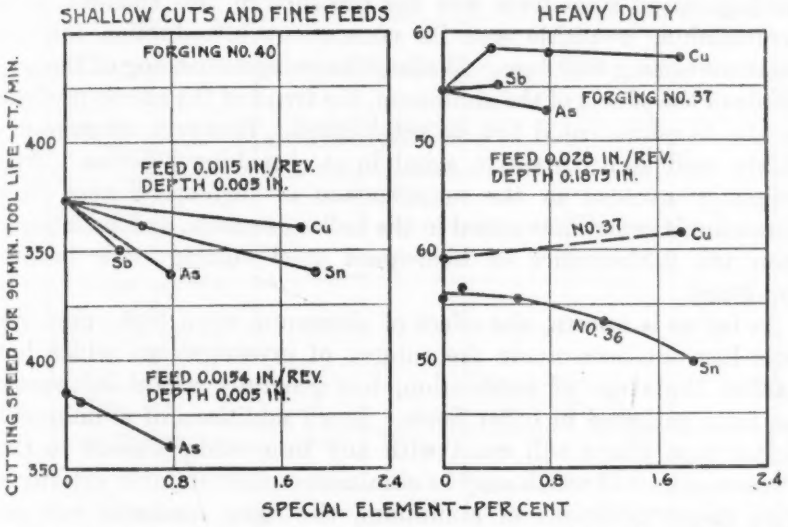

FIGURE 22.—*Effects of arsenic, antimony, copper, and tin on the cutting speed of high-speed steel tools under shallow cuts and under heavy duty*

Compositions of the tools and their heat treatment are given in Table 2; properties of the forgings are given in Table 3. All tests were made dry.

be expected, since any tendency to promote crumbling of the cutting edge, which would be observed with shallow cuts when the frictional temperatures are low, would probably be masked by the softening of the steel at the high operating temperatures encountered in rough turning.

In addition to lathe tool tests, Rockwell hardness tests were made on samples quenched and tempered in various ways, and with few exceptions the hardness of the steels containing the different impurities was practically the same as that of the steels without these impurities similarly treated. The addition of 0.15 per cent tin increased the hardness of the steel as oil-quenched from 2,000° F.; when the proportion of tin was raised to 0.57 per cent, there was an additional

increase in the hardness, but with further increase in tin the hardness decreased slightly.

The additions of antimony, arsenic, copper, or tin produced no outstanding changes in the structures of the high-speed steel tools, although there was a tendency for increase in grain size with increase in copper content and a decrease in grain size as the proportions of antimony, arsenic, or tin were increased. Typical structures are shown in a preliminary report referred to in footnote 35 (p. 872) of the text.

7. STEELS WITH ALUMINUM

The principal reason for considering the effects of aluminum upon the high-speed steel tools was the presence of this element in the ferrotitanium available and its consequent introduction into the steels containing titanium. Without knowing something of the magnitude of the effects of the aluminum, the trend of the effects produced by the titanium could not be established. However, aluminum is widely used as a corrective agent in steel-making practice. While ordinarily avoided in the manufacture of high-speed tool steels, aluminum is sometimes added in the ladles or molds, and its influence upon the performance of high-speed steel cutting tools becomes important.

As far as is known, the effect of aluminum upon high-speed steel tools has not been made the subject of investigations which have reached the stage of publication, but generally useful information has been gathered in other fields. Small additions of aluminum to molten iron alloys will react with any iron oxide present to form alumina, a part of which may be eliminated under suitable conditions. With larger additions of aluminum, the same reactions can take place, but the larger part of the aluminum is dissolved in the steel as aluminum.

According to Guillet,[36] the presence of aluminum in iron-carbon alloys—

> has the effect of preventing the pearlite from assuming its ordinary forms; it is, in a manner, contorted, and forms little nodules which are the more easily colored by picric acid and the more closely resemble troostite in proportion as the percentage of aluminum increases. With a very high percentage of aluminum it is even possible to have free cementite formed in a hypoeutectoid steel. * * *
>
> Quenching transforms only the nodules of the preexisting pearlite, giving place to martensite, generally encircled around its edges by troostite. The result is always the same, no matter what the temperature of quenching. It must, therefore, be recognized that the iron-aluminum solution is incapable of dissolving carbon.
>
> From the mechanical point of view quenching has no effect except when the pearlite exhibits its ordinary structure; that is to say, so long as the aluminum is below 3 per cent.

[36] L. Guillet, Quarternary Steels, J., Iron and Steel Inst., No. 2, p. 1; 1906.

Aluminum was found to increase the tensile strength and decrease the elongation and reduction of area, slowly at first but rapidly when the aluminum was raised above 3 or 4 per cent; the brittleness also increased rapidly.

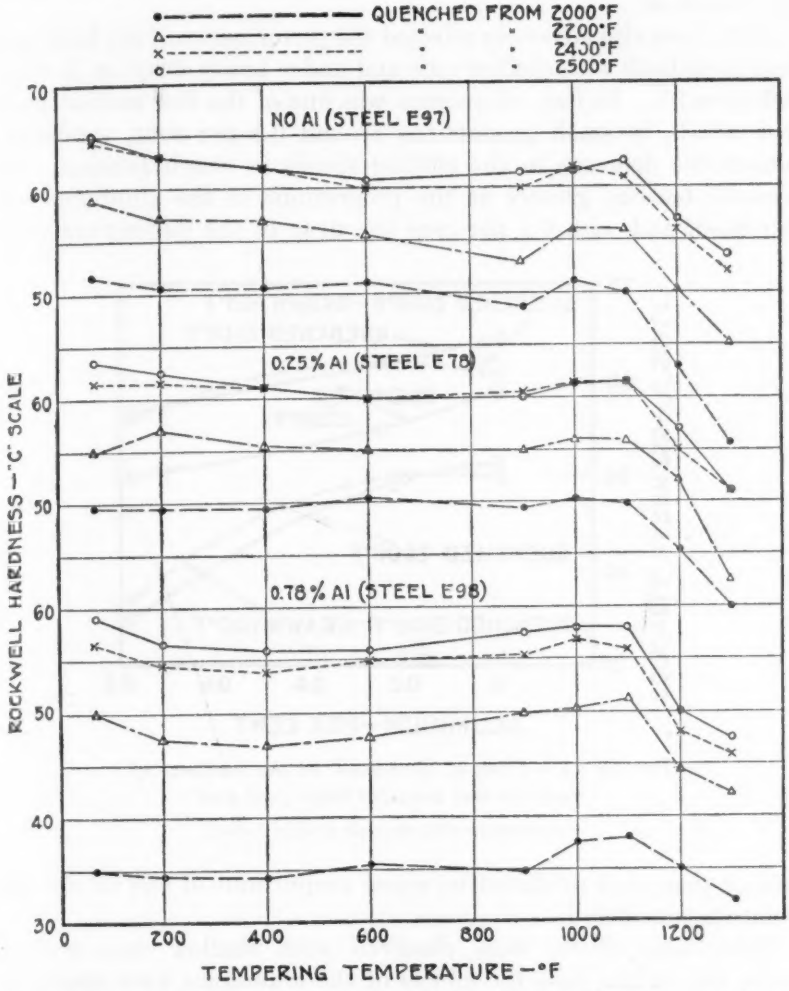

FIGURE 23.—*Hardness of high-speed steels containing different proportions of aluminum when subjected to different heat treatments*

Compositions of the steels are given in Table 2.

The effects produced in the high-speed steels by aluminum were similar in some respects to those described by Guillet for carbon steels but were observed with smaller additions of aluminum. As is shown in Figures 23 and 24, the hardness of the steels containing aluminum decreased, after either quenching or quenching followed by tempering, as the proportion of aluminum was raised from prac-

tically 0 to 0.8 per cent. However, the numerical values of the hardness obtained were quite largely dependent upon the quenching temperature. In effect, the entire set of hardness curves (fig. 23) was shifted to lower values of hardness as the proportion of aluminum was increased.

Aluminum also adversely affected the performance of the high-speed steel tools both with shallow cuts and under heavy duty, as is shown in Figure 25. In fact, aluminum was one of the few metals considered which, in small proportions around 0.3 per cent, produced a measurable decrease in the cutting speeds in rough turning. This decrease became greater as the proportions of the aluminum were increased, and with 0.8 per cent the drop in the cutting speed was

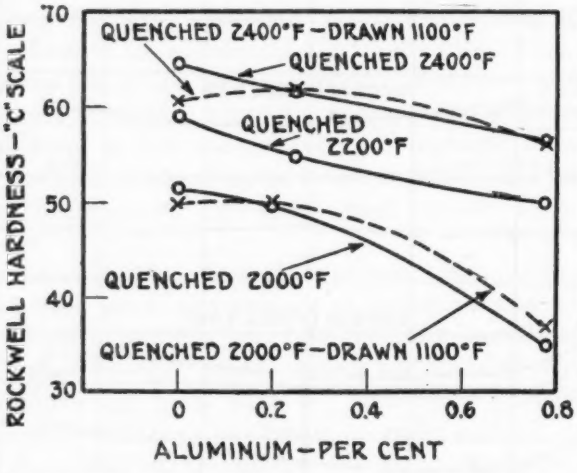

FIGURE 24.—*Effect of aluminum on the hardness of quenched and tempered high-speed steel*

Compositions of the steels are given in Table 2.

greater than that produced by equal proportions of any of the other elements considered.

Deleterious effects were observed with shallow cuts and fine feeds, but in this case the effects of the aluminum were about on a par with those of arsenic and antimony and more marked than those of either tin or copper.

The reasons for decrease in the hardness and the tool performance with increase in the aluminum have not been established, but the structures of the steels throw some light on this subject.

The structure of one of the quenched and untempered high-speed steel tools containing about 0.8 per cent aluminum was, perhaps, the most illuminating since it showed characteristics somewhat similar to those described by Guillet for carbon steels. As is shown in Figure 26, *c*, a large number of undissolved particles were found at the aus-

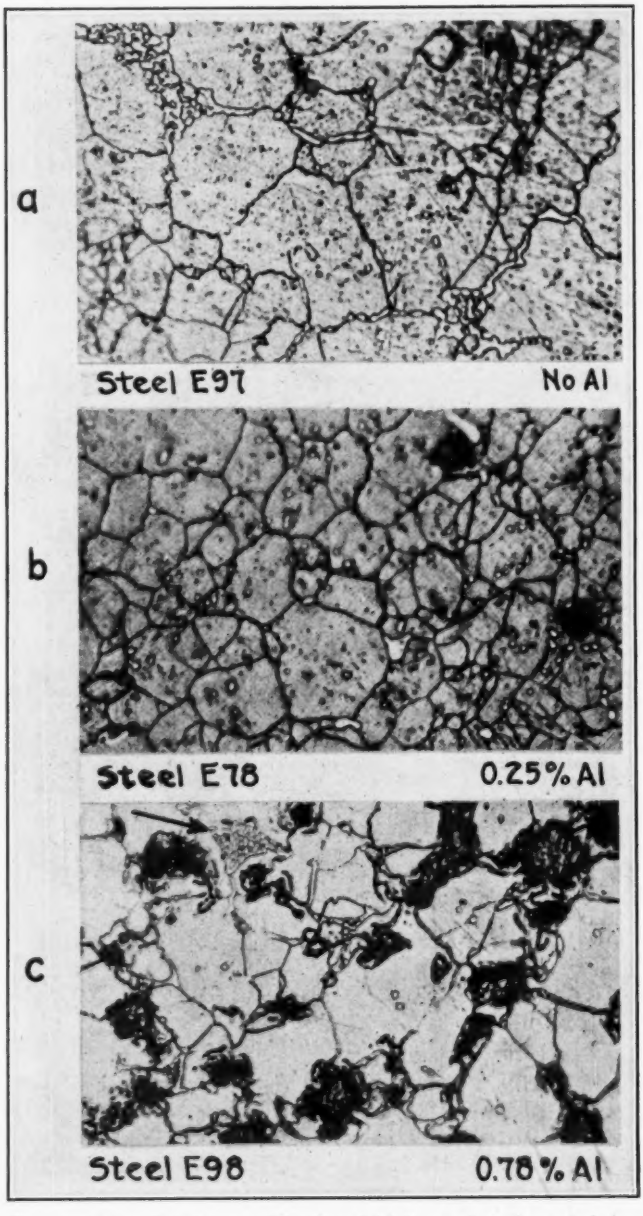

FIGURE 26.—*Structures of hardened high-speed steels containing different proportions of aluminum.* × *750*

Samples oil quenched from 2,350° F. not tempered; etched with 2 per cent HNO_3 in alcohol.

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tenite grain boundaries, and the outer areas of the zones of concentration of these undissolved constituents were encircled by more darkly etched areas, perhaps representing a structure comparable to troostite.

Such a large number of undissolved aggregates are not ordinarily found in the customary high-speed steels quenched from comparable temperatures (fig. 26, *a*) and must represent a decreased dissolving power of the austenite (matrix) for one or more of the elements, carbon, chromium, tungsten, and vanadium which constitute the key elements in the steels under consideration.

In other words, the 0.8 per cent aluminum has decreased the solubility in the austenite of one or more of the elements mentioned and through the resultant precipitation has lowered the hardness and other useful properties of the steel. Along with this precipitation is evidence

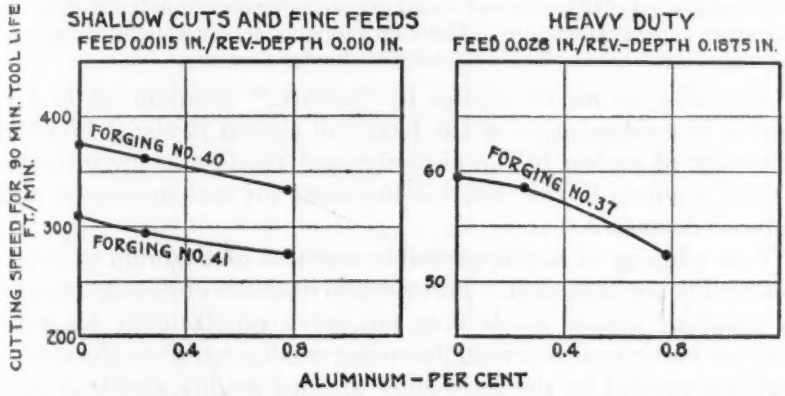

FIGURE 25.—*Effect of aluminum on the cutting speed of high-speed steel tools under shallow cuts and under heavy duty*

Compositions of the tools and their heat treatment are given in Table 2; properties of the forgings are given in Table 3. All tests were made dry.

of the formation of low melting point eutectics (see arrow, fig. 26, *c*) which are only evident in the customary high-speed steels as cast or when overheated. Such partial melting is an added source of danger in high-speed steel tools and probably contributed in a measurable degree to the poor performance described.

The exact nature of the compounds and the low melting eutectics has not been determined, but the observed structures, hardness, tool performance, and poor hot working properties previously described clearly show the importance of guarding against the introduction of more than very small proportions of aluminum in high-speed tool steels.

8. STEELS WITH TITANIUM

So far titanium has not shown much promise as an alloying element in steels and is now mainly used as one of a number of corrective agents (scavengers) in steel making, and in this latter field it seems

to combine most readily with oxygen and nitrogen. The present situation regarding the applications and effects of titanium in steels is about as described by Gillett and Mack,[37] as follows:

> The alloying effect of titanium seems to be negligible, its only use being as a scavenger to remove oxygen and, perhaps, nitrogen. It seems to reduce segregation of carbon and of impurities. Some of the data cited by the advocates of titanium [38] to show its value as a scavenger lie well within the range of results obtained without it, and the proof of its usefulness is seldom clear-cut. A thorough study [39] of the deoxidation of rail steel by titanium and by silicon has been made by the Bureau of Standards. This shows that the action of titanium in restraining segregation is definitely shown only in the top of the ingot; that the average mechnaical properties of the steel are not noticeably altered by titanium; and that the claim that the oxidation products of titanium do not remain in the steel is not in accord with the facts.
>
> Stoughton [40] believes that titanium causes occluded oxidized materials which would cause inclusions to be more readily separated from the melt, and Giolitti [41] mentions the use of titanium and vanadium as having specific action in developing fine grain on heat treatment. Titanium probably serves a useful purpose as a scavenger, but it has no place in a list of true alloying elements.

According to recent studies by Tamaru,[42] titanium up to 4 per cent is in solid solution in the ferrite of carbon steels; it lowers the solubility of carbon in the austenite and accelerates graphitization. As the titanium in the steel was increased the carbon content of the eutectic decreased.

True alloying of any appreciable amounts of titanium in steels is not readily accomplished. Ferrocarbon titanium ordinarily employed in titanium treated steels does not serve satisfactorily for such a purpose under ordinary manufacturing conditions, since the titanium carbides present in the ferro-alloy are not readily dissolved in the steel. Even with so-called carbon-free ferrotitanium favorable conditions were found to be necessary for a reasonably good recovery of the added titanium.

In the five high-speed steels containing titanium, which are listed in Table 2, the titanium was added to and did not replace any portion of the elements ordinarily present. Three of these steels contained about the customary proportions of carbon, while two others were much higher in carbon content.

With 0.6 to 0.8 per cent carbon and 0.4 per cent or less of titanium the hardness of the steels increased generally with increase in the quenching temperature in much the same manner as corresponding

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[37] H. W. Gillett and E. L. Mack, Molybdenum, Cerium, and Related Alloy Steels, Chemical Catalog Co. (Inc.), New York; 1925.

[38] Titanium Alloy Manufacturing Co., Titanium, Its Effects on Steel. Booklet; 1919. Ferro-Carbon Titanium in Steel Making. Booklet; 1916.

[39] G. K. Burgess and G. W. Quick, A Comparison of the Deoxidation Effects of Titanium and Silicon on the Properties of Rail Steel, B. S. Tech. Paper No. 241; 1923.

[40] B. Stoughton, The Metallurgy of Iron and Steel, McGraw-Hill Book Co. (Inc.), p. 206; 1923.

[41] F. Giolitti, Steel Castings of High Strength and Toughness, Chem. Met. Eng., **24**, p. 161; 1921.

[42] K. Tamaru, On the Equilibrium Diagram of the System Iron-Carbon-Titanium, Sci. Repts. Tohoku Imp. Univ., Series I, **15**, No. 1, p. 25; March, 1925.

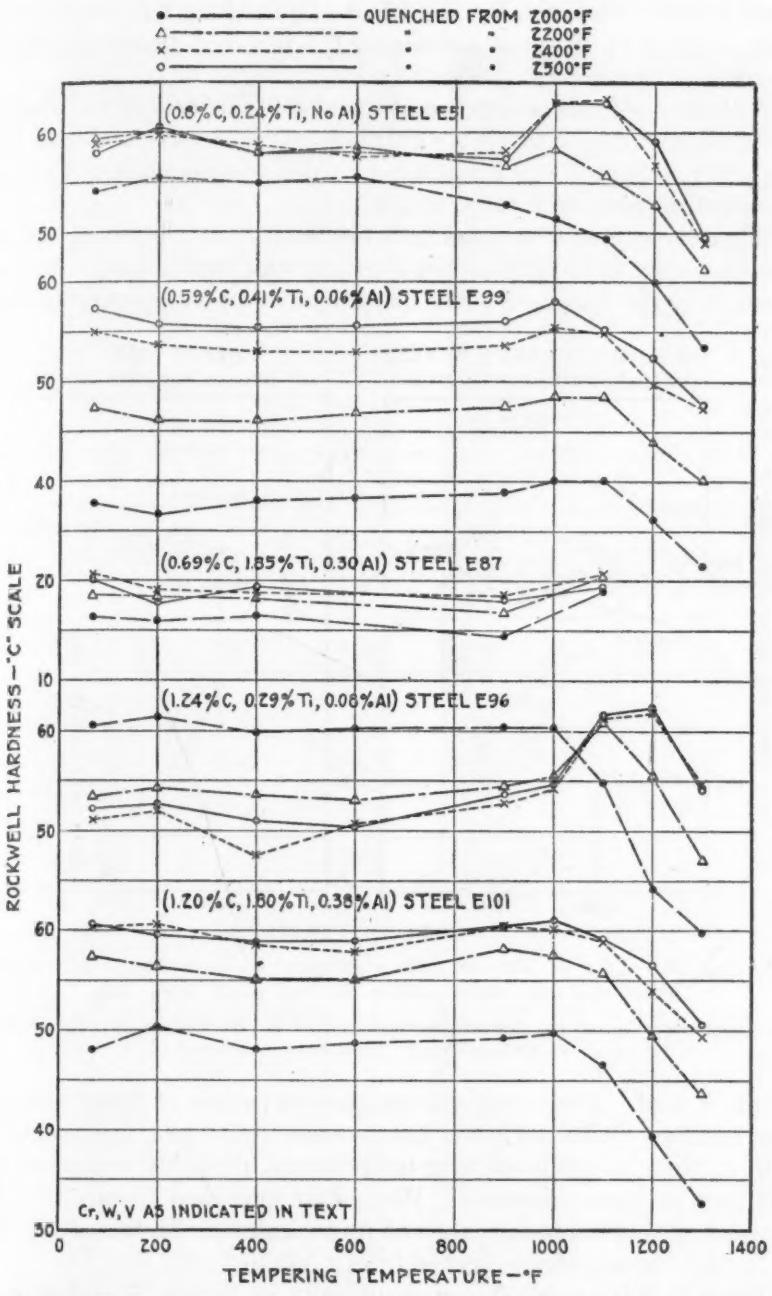

FIGURE 27.—*Hardness of high-speed steels containing different proportions of titanium (and aluminum) when subjected to different heat treatments*

Complete chemical compositions are reported in Table 2.

steels without titanium, but the effect of quenching temperature was more marked in the steel containing 0.4 per cent titanium than in that with 0.24 per cent. (Fig. 27.)

With any one quenching temperature the hardness of the untempered samples decreased as the titanium was increased, and with 1.85 per cent titanium the steel would not harden when quenched from any temperature between 2,000 and 2,500° F.

When the carbon was raised from around 0.7 to 1.2 per cent and the titanium kept at around 1.8 per cent, the steel again hardened upon quenching, the hardness being dependent upon the quenching tem-

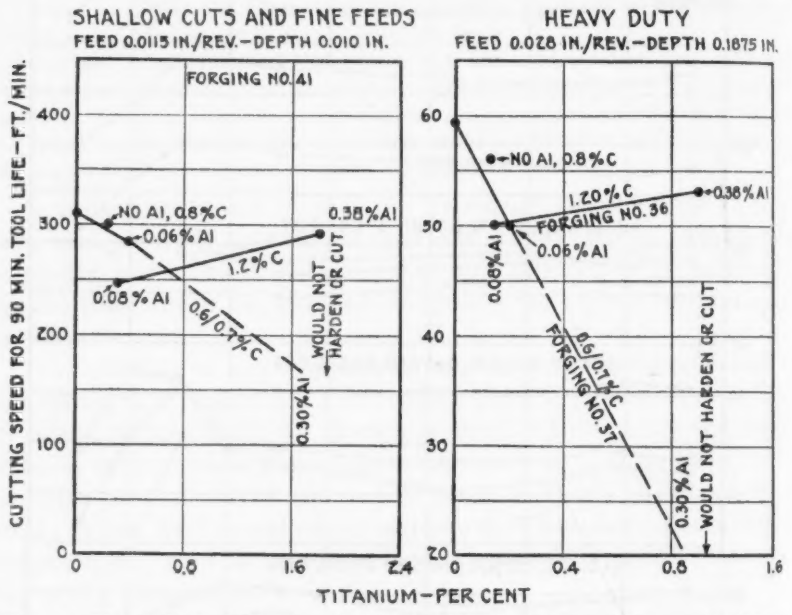

FIGURE 28.—*Effect of titanium (plus aluminum) on the cutting speed of high-speed steel tools under shallow cuts and under heavy duty*

Compositions of the tools and their heat treatment are given in Table 2; properties of the forgings are given in Table 3. All tests were made dry.

perature used. However, with comparable carbon (1.2 per cent) and less titanium (0.29 per cent) the hardness on quenching decreased with increase in the quenching temperature, probably indicating the retention of more austenite. When first quenched from 2,000° F., samples of this latter steel showed no rehardening on tempering (fig. 27) as did the samples quenched from 2,300 to 2,500° F.

These results are all shown graphically in Figure 27 and indicate that the hardness of the quenched steels was not solely a function of the proportion of titanium but depended upon the relative amounts of titanium and carbon present.

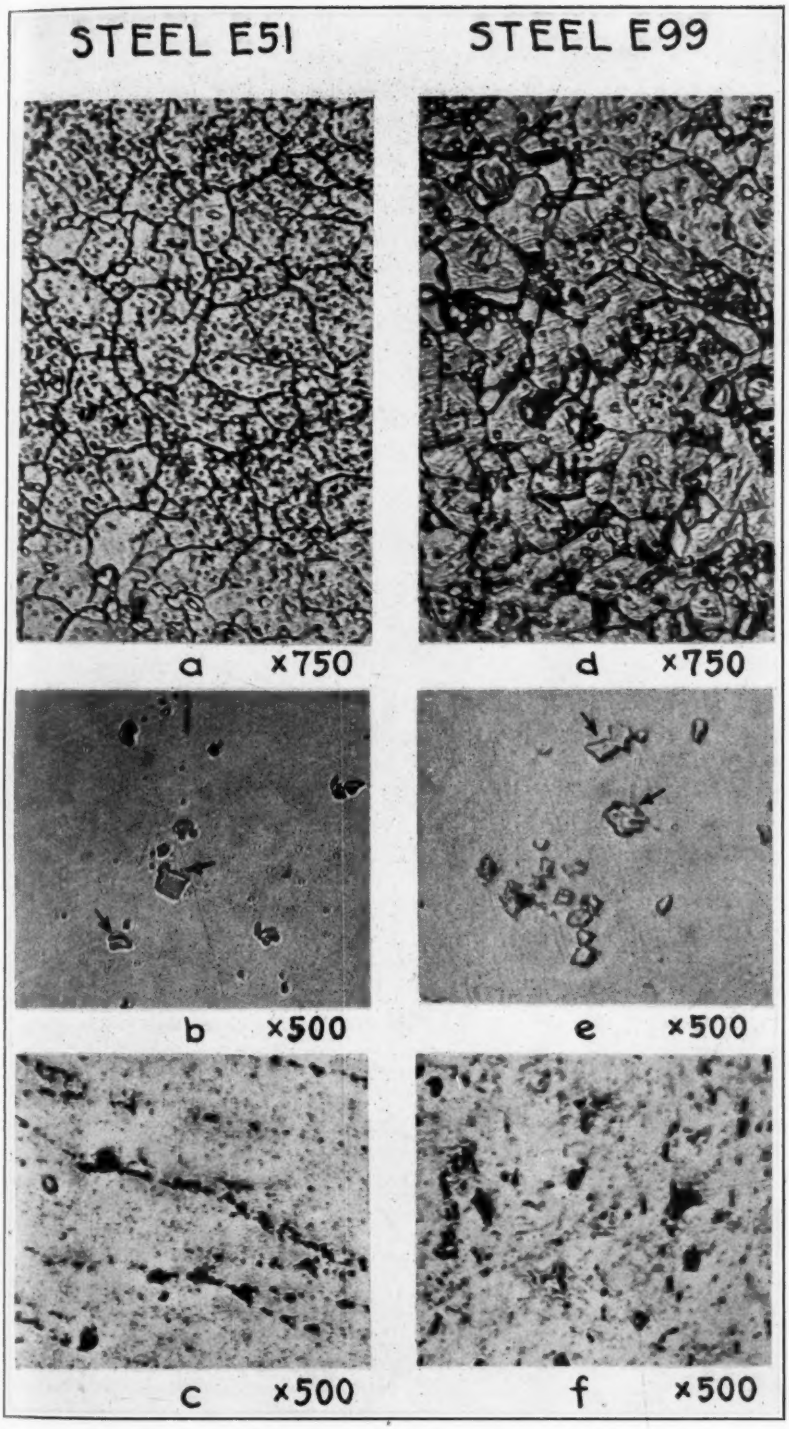

FIGURE 29.—*Structures of hardened high-speed steels containing different proportions of titanium (and aluminum)*

Compositions of the steels are given in Table 2; (*a*) and (*d*), etched with 5 per cent HNO_3 in alcohol; (*b*) and (*e*), unetched; (*c*) and (*f*), etched in boiling solution of $KMnO_4$ (4 g), NaOH (4 g) in 100 ml H_2O. Samples first oil quenched from 2,350° F.

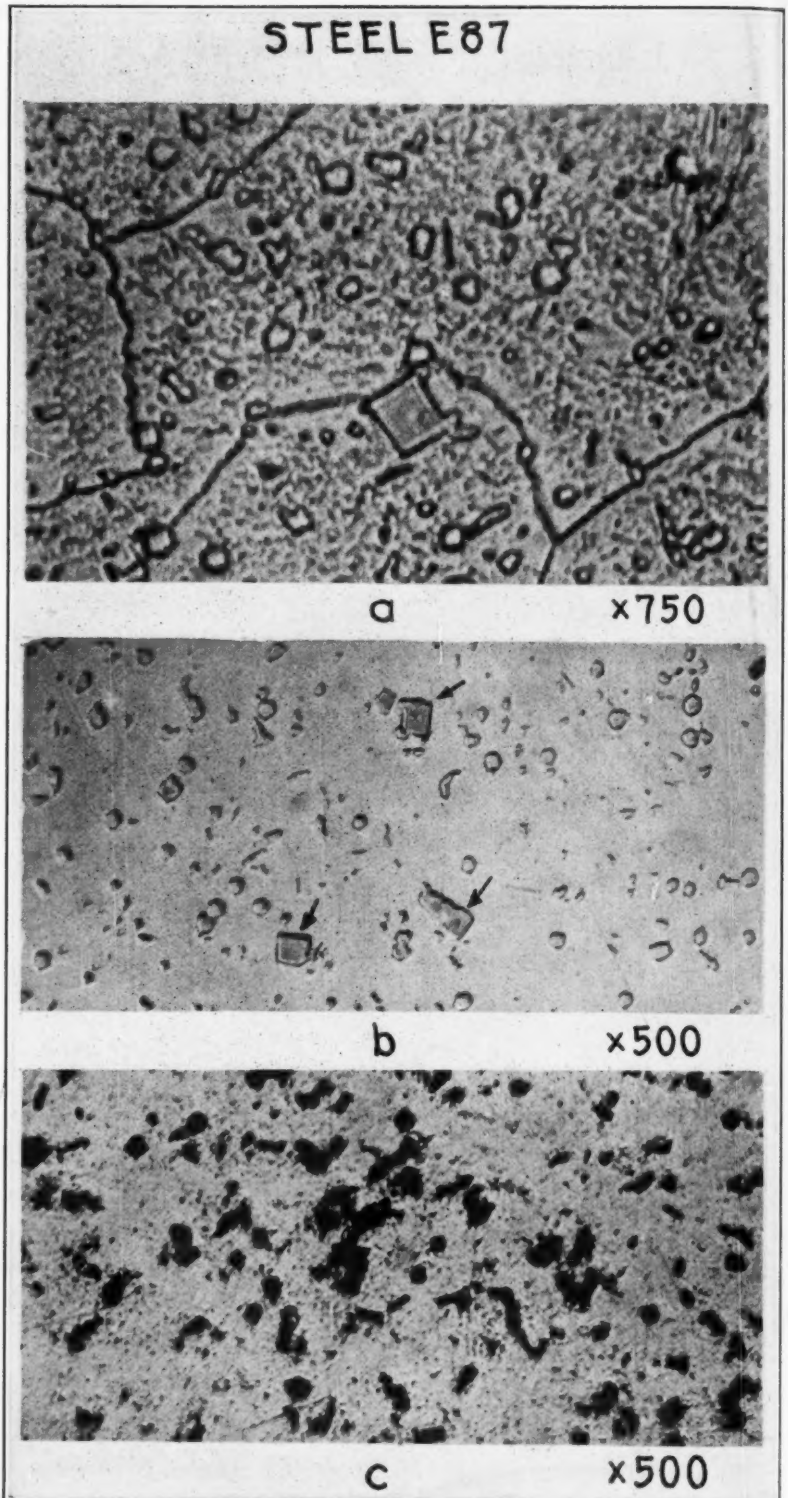

FIGURE 30.—*Structure of one of the high-speed steels containing titanium as oil quenched from 2,350° F.*

Chemical composition is given in Table 2; (*a*), etched with 5 per cent HNO_3 in alcohol; (*b*), unetched; (*c*), etched in boiling solution of $KMnO_4$ (4 g), NaOH (4 g) in 100 ml H_2O.

The performance of the high-speed steel tools containing titanium and the customary proportions of carbon was disappointing. As is shown in Figure 28, the cutting speeds decreased both with shallow cuts and under heavy duty as the titanium was increased. The steel with about 0.7 per cent carbon and 1.8 per cent titanium which would not harden also failed to cut at the speeds used in the experiments. Tests at lower speeds might have resulted in a measurable duration of cut, but for all practical purposes the steel referred to did not have cutting properties comparable to high-speed tool steels.

When the carbon in the steels was raised to 1.2 per cent, increase in titanium from about 0.3 to 1.8 per cent resulted in improved performance both under shallow cuts and under heavy duty. However, the performance of tools of steel E96 may not be characteristic of the reported composition for reasons later explained, but in no case did the steels containing titanium give as good performance as the high-speed steels of customary composition without titanium.

It should be noted that increase in the proportions of titanium resulted in an increase in the proportions of aluminum in the high-speed steels. Aluminum has already been shown to have a highly deleterious effect upon the performance of high-speed steel tools, and therefore the changes in the cutting speeds shown in Figure 28 can not be ascribed entirely to titanium.

The reductions in the cutting speeds produced by the different proportions of aluminum found in the titanium high-speed steels can be estimated from data given in Figure 25, and if these reductions in the cutting speed are subtracted from those produced by titanium plus aluminum given in Figure 28 the effects of titanium alone can be estimated. These calculations are incorporated in Table 15 and show that appreciable proportions of titanium exerted a highly deleterious effect upon the cutting speeds, both with shallow cuts and under heavy duty except in the case of the two high-carbon steels.

While the effects of titanium alone, as given in Table 15, are smaller than those shown in Figure 28, the estimated corrections for aluminum did not change the general trends shown in Figure 28.

All of the titanium steels contained characteristic pink or orange colored titanium inclusions, probably nitrides or cyanonitrides. (Figs. 29(*b*), 29(*c*), 30(*b*), 31(*b*), and 31(*c*).) The structure shown in Figure 30(*a*) for steel E87, which could not be hardened appreciably by heat treatment, is probably a solid solution of alpha iron, titanium, and aluminum plus a large number of carbides, tungstides, titanium inclusions and possibly other undissolved particles.

TABLE 15.—*Effects of titanium in high-speed tool steels estimated from data given in Figures 25 and 28*

Steel No.	Partial chemical composition [1]			Reduction in cutting speed [2] produced by—					
				Ti+Al (from fig. 28)		Equivalent Al (from fig. 25)		Ti [(Ti+Al)−Al=Ti]	
	C	Ti	Al	Shallow cuts	Heavy duty	Shallow cuts	Heavy duty	Shallow cuts	Heavy duty
	Per cent	*Per cent*	*Per cent*						
E51	0.80	0.24	------	6	−2	0	------	6	−2
E99	.59	.41	0.06	27	10	3	0.5	24	9.5
E87 [3]	.69	1.85	.30	310	60	15	1.5	295	58.5
E96	1.24	.29	.08	63	8	4	.5	59	7.5
E101	1.20	1.80	.38	18	4	20	2	−2	2

[1] For complete composition and heat treatment of the tools see Table 2.
[2] For 90-minute tool life under the conditions indicated in Figures 25 and 28.
[3] Would not cut.

As the titanium content of the steels was increased, the number of undissolved particles also increased, as is shown in Figures 29 (*c*), 29 (*f*), and 30 (*c*) for the steels containing 0.6 to 0.8 per cent carbon and in Figures 31 (*c*) and 31 (*f*) for the steels containing 1.2 per cent carbon. The darkened patches between the grains in the etched sample of steel E101, shown in Figure 31 (*d*), are probably due to the aluminum present and resemble features shown in Figure 26 (*c*) for high-speed steel containing about 0.8 per cent aluminum without titanium.

The structures shown in Figures 29, 30, and 31 indicate that titanium decreases the dissolving capacity of the austenite for the elements which ordinarily are responsible for the characteristic properties of high-speed steels through their solution at high hardening temperatures.

However, titanium is known to form carbides very readily, and in the presence of varying amounts of carbon different effects may be produced. In the presence of high carbon the titanium will probably first form carbides, and any titanium remaining may then go directly into solution in the iron. This, of course, assumes that there is an excess of titanium available. In the high-speed steel containing 1.2 per cent carbon and 1.8 per cent titanium (E101) the high carbon restored the ability of the steel to harden upon quenching and gave a tool performance nearly equal to that of high-speed steels of customary composition. However, these benefits were probably not derived from any useful alloying effects of titanium, but probably were produced by putting the titanium in a less harmful condition, (carbides instead of solution in the iron), so that the chromium, tungsten, and vanadium could act in their normal manner.

The low cutting speed of the high carbon high-speed steel tools containing only 0.29 per cent titanium can not be explained at this time but was probably due either to the high carbon in the absence of appreciable amounts of titanium or to peculiarities of the particular heat from which the tools were prepared. The recovery of titanium in this steel was low, its working properties were poor (fig. 17), and, as has already been pointed out, it probably had areas of segregation.

Titanium may, therefore, be considered to be an undesirable addition to the customary high-speed steel compositions since it decreases the dissolving power of the austenite for those compounds which must be brought into solution to produce the properties characteristic of ordinary high-speed steels. Its interference is lessened, probably through the formation of less harmful carbides (instead of solution as titanium in the austenite), by increasing the carbon content of the steel. The amount of carbon required will probably vary with the titanium content and was in the neighborhood of 1.2 per cent carbon for 1.8 per cent titanium.

9. STEELS WITH TANTALUM

During the year 1924, while a study was being made of the chemical composition of heavy-duty lathe tools, rumors were received that promising results were being obtained in England with high-speed steels containing tantalum. While no details were available and no performance records could be obtained at that time, a number of experimental steels were made containing different proportions of tantalum and tested in comparison with high-speed steels of customary composition. The tests were made with deep cuts and coarse feeds, but more recently the same steels were tested under shallow cuts and fine feeds, and a summary of all of the results is now given for the first time.

A report of the preliminary experiments was made in 1925,[43] and discussion of the results brought to light some further information on tantalum in tool steels. One British metallurgist reported [44] that he had made a series of steels presumably with 0.6 per cent carbon, some chromium, and from 1 to 6 per cent tantalum. The steel with 6 per cent tantalum showed properties somewhat similar to the "red hardness" of ordinary high-speed tool steels. In further work, a steel containing about 6 per cent tungsten and 6 per cent tantalum was said to have had about 75 per cent cutting "efficiency" in comparison with the usual tungsten steels.

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[43] See footnote 24, p. 863.

[44] Private communication.

J. P. Gill [45] reported that during the years 1920–21 the firm with which he was associated had spent some time in a study of tantalum in high-speed tool steels. He stated that—

> this company probably made up as many as 100 different composition high-speed steels containing tantalum, tungsten, chromium, vanadium, and cobalt. Some of the heats made were as large as 7,000 pounds. Lathe tests were run, many physical tests were made, and it was found that several of the steels compared favorably with some of the regular high-speed steels in commercial use to-day, but these steels were no better than the same steels without tantalum. We did not find any steels that were better than the regular high-speed steels. Many things were learned in regard to the use of tantalum. The manner of introducing the tantalum into the steel and the form of the tantalum in the alloy apparently affected the results. The tantalum steels were found to be very dirty and full of oxides even when melted under the best of conditions. Even in view of this fact, however, the tantalum steels seemed to be tougher than the standard types of high-speed steel.

Studies of tantalum in carbon steels have been reported by Guillet,[46] Portevin,[47] and others,[48] but these investigations do not throw much light upon the subject under discussion. Apparently tantalum up to at least 8 per cent in iron-carbon alloys is in solution in the ferrite, and with carbon up to 0.6 per cent the steels are pearlitic on normal slow cooling and martensitic after quenching. The effects of tantalum on steels which are suitable for cutting tools are not generally known, although a few patents, typified by that granted to F. T. McCurdy,[49] indicate that tantalum may be useful in this field.

The seven steels containing tantalum that were tested fall into three classes. Steel E23 (Table 2) is a chromium-tantalum steel similar to one previously mentioned as having been made experimentally in England. Steel E42 is a chromium-tungsten-vanadium steel in which about 6 per cent of tungsten was replaced by 6 per cent of tantalum. The steels E43, E44, and E16 contained the usual proportions of special elements except that the vanadium was replaced by different proportions of tantalum. The results obtained with these three steels suggested that increased carbon might improve the properties, and accordingly two similar steels were made, E45 and E100 (Table 2), with 0.9 and 1.4 per cent carbon, respectively.

A study was first made of the hardness of the different steels after different heat treatments and developed some interesting characteristics. There was no evidence of rehardening on tempering of the chromium-tantalum steel E23, as is shown in Figure 32.

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[45] Discussion of the report referred to in footnote 24, p. 863.

[46] L. Guillet, Sur les proprietes et la constitution des aciers au tantale, Comptes Rendus, **145**, p. 327; 1907.

[47] A. M. Portevin, Contribution to the Study of the Special Ternary Steels, Carnegie Scholarship Memoirs, **1**, p. 230; 1919.

[48] An Investigation of Tantalum Steels (for G. G. Blackwell Sons & Co. (Ltd.), Liverpool, England). The Iron & Coal Trades Rev., **78**, p. 933; 1909.

[49] United States patent 1449338, Mar. 20, 1923.

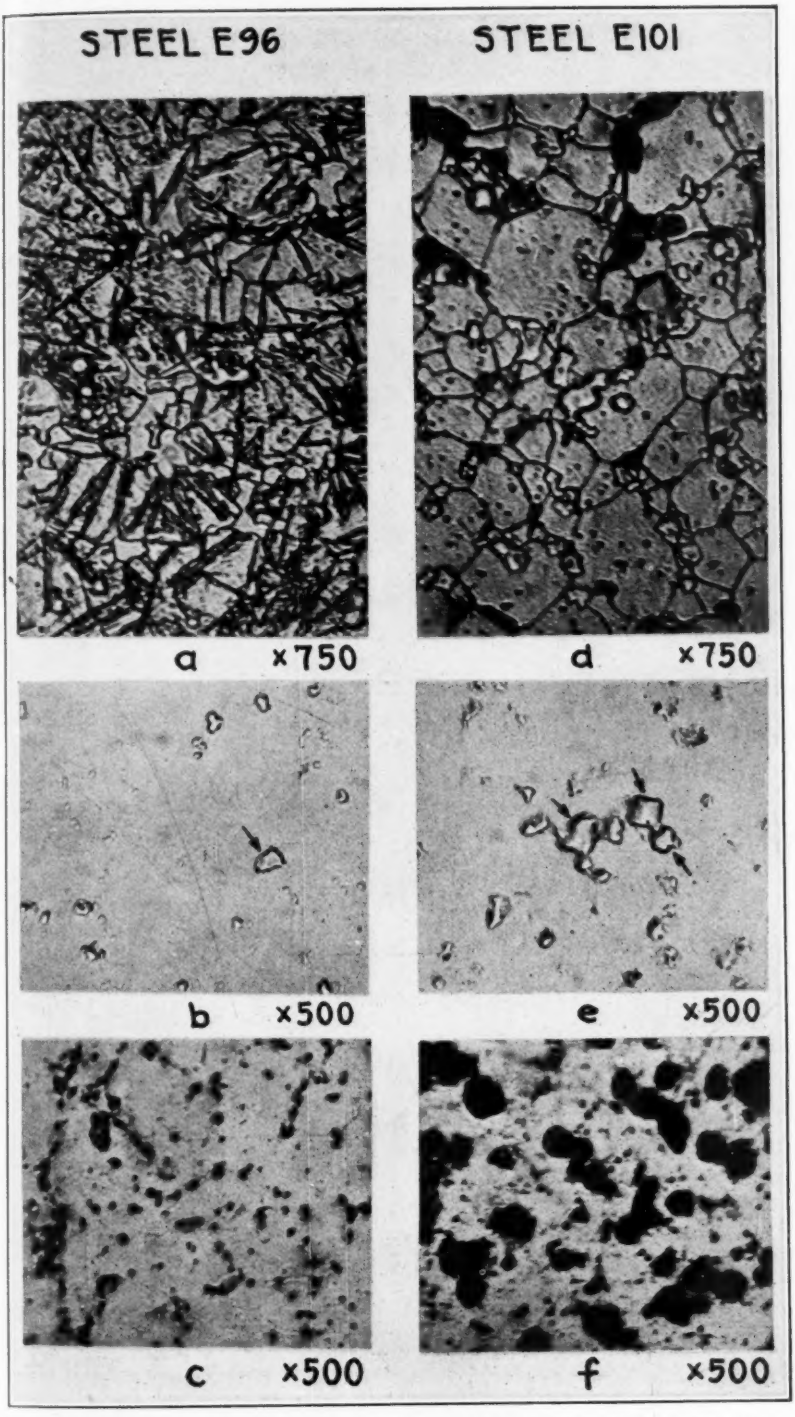

FIGURE 31.—*Structures of hardened high-speed steels containing about 1.2 per cent C and different proportions of titanium (and aluminum)*

Compositions of the steels are given in Table 2; (*a*) and (*d*), etched with 5 per cent HNO_3 in alcohol; (*b*) and (*e*), unetched; (*c*) and (*f*), etched in boiling solution of $KMnO_4$ (4 g), NaOH (4 g) in 100 ml H_2O. Samples first oil quenched from 2,350° F.

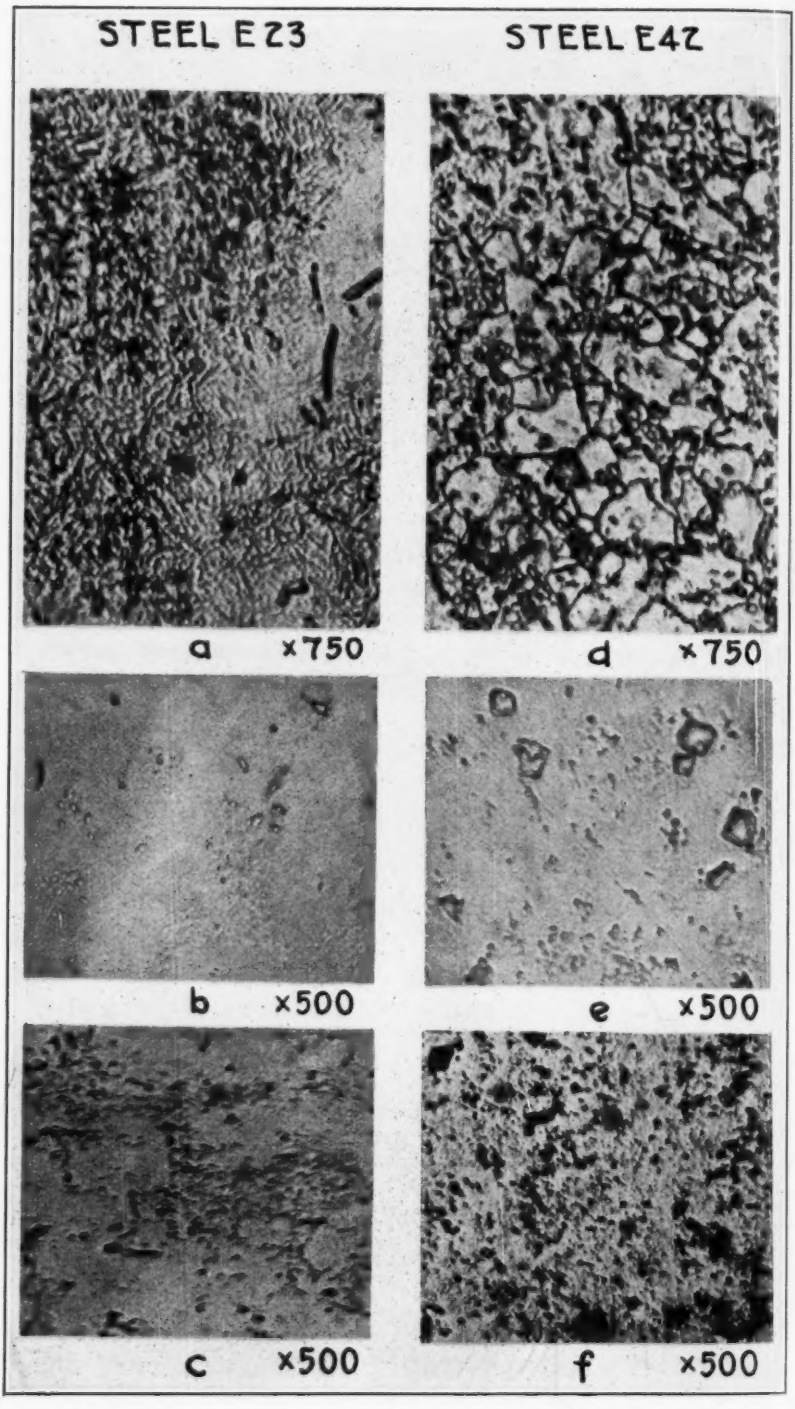

FIGURE 33.—*Structures of the chromium-tantalum steel and the chromium-tungsten-tantalum-vanadium steel as oil quenched from 2,350° F.*

Compositions of the steels are given in Table 2; (*a*) and (*d*), etched with 5 per cent HNO_3 in alcohol; (*b*) and (*e*), unetched; (*c*) and (*f*), etched in boiling solution of $KMnO_4$ (4 g), NaOH (4 g) in 100 ml H_2O.

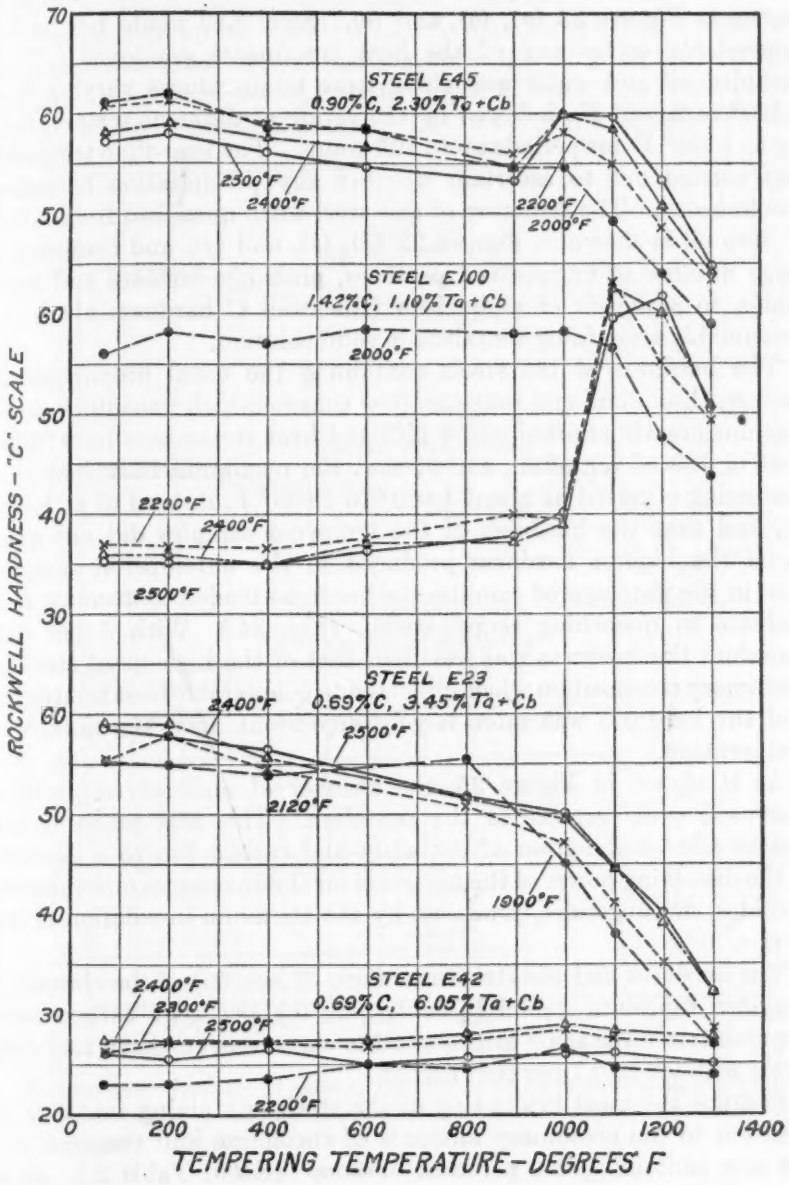

FIGURE 32.—*Hardness of some of the high-speed steels containing different proportions of tantalum (+columbium) when subjected to different heat treatments*

Compositions of the steels are given in Table 2. Quenching temperatures are shown in the body of the chart.

The hardened samples appeared to be predominately martensitic with some undissolved particles, probably chromium carbides, as is shown in Figures 33 (*a*), (*b*), and (*c*). Steel E42 would not harden appreciably under any of the heat treatments employed. These included oil and water quenching from temperatures varying from 1,500° to 2,500° F., followed by tempering at different temperatures up to 1,400° F. for periods up to 195 hours. The long-time tempering was carried out to ascertain whether any precipitation hardening would occur. The structure of this steel when quenched from 2,350° F. into oil is shown in Figures 33 (*d*), (*e*), and (*f*), and comprised a large number of undissolved particles, probably carbides and tungstides, in a matrix of alpha iron (Rockwell C hardness about 27) presumably containing tantalum in solid solution.

The hardness of the steels containing the usual proportions of carbon, chromium, and tungsten (low tungsten-high vanadium steels) was not greatly affected under different heat treatments by 0.75 per cent or less of tantalum, except that the maximum rehardening on tempering occurred at about 1,000° to 1,050° F. instead of at 1,100° F., and that the hardness of the tempered samples did not quite equal the highest hardness produced in the untempered samples. Also in the untempered samples the hardness tended to decrease with increase in quenching temperature. (Fig. 34.) With 5 per cent tantalum the hardness was less than that of the high-speed steels of customary composition when subjected to comparable heat treatments and the hardness was more largely dependent upon the quenching temperature.

As is shown in Figure 35, the number of undissolved particles increased with increase in the tantalum. This was probably not due to any combination of tantalum and carbon but to a decrease in the dissolving power of the austenite for the chromium and tungsten carbides, or tungstides, produced by the tantalum in solution in the iron.

The hardness and the structures (figs. 32 and 36) of the chromium tungsten tantalum steel E45 containing 0.9 per cent carbon were approximately the same as those of the chromium tungsten tantalum steels with 0.6 to 0.7 per cent carbon.

Perhaps the most interesting of the steels containing tantalum in addition to the customary amounts of chromium and tungsten was the one containing 1.4 per cent carbon. (E100, Table 2.) As is shown in Figure 32, this steel had a Rockwell C scale hardness of only about 36 when oil quenched from temperatures between 2,200° and 2,500° F. When hardened from a lower temperature, 2,000° F., its hardness was about 56 and was not appreciably changed upon subsequent tempering at temperatures up to 1,100° F.

The samples which did not harden when oil quenched from 2,200° to 2,500° F. did not harden appreciably when subsequently tempered at temperatures up to 1,000° F., but with increase in tempering temperature to 1,100° F. showed a surprisingly large increase in the hardness. This increase on the Rockwell C scale was from about 40 to 62, a difference of 22 points. The untempered samples showed

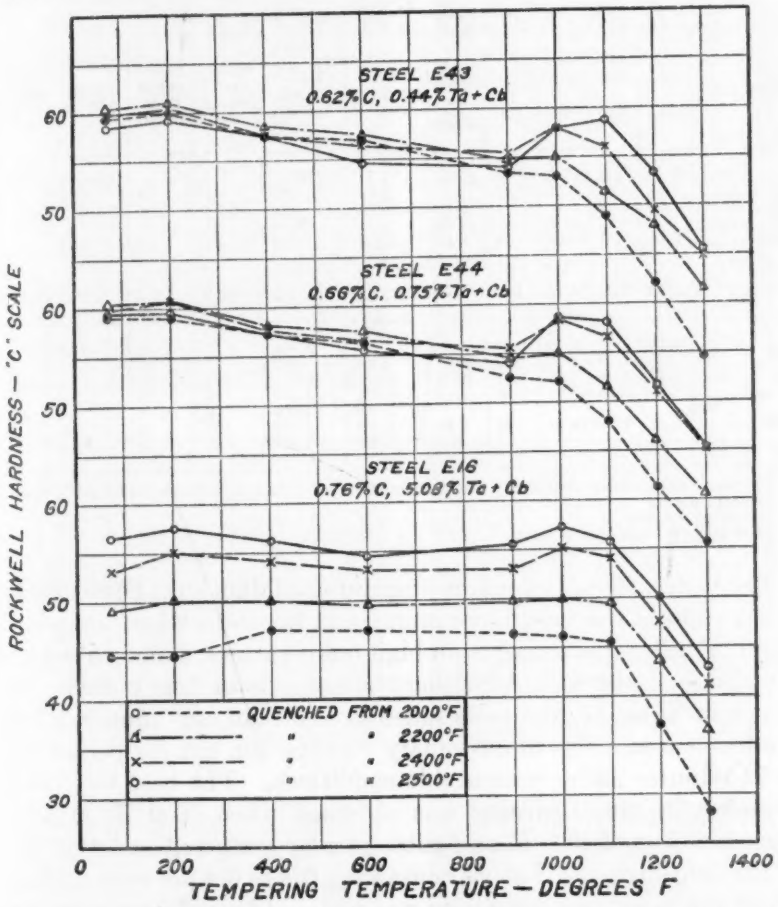

FIGURE 34.—*Hardness of some of the high-speed steels containing different proportions of tantalum (+columbium) when subjected to different heat treatments*

Compositions of the steels are given in Table 2.

an austenitic matrix with numerous undissolved particles at the austenite grain boundaries, as is shown in Figures 36 (*d*), (*e*), and (*f*).

None of the steels containing tantalum showed as good performance as the high-speed steels of customary compositions, either with shallow cuts and fine feeds or under heavy duty. Steel E42, which would not harden, also failed to cut. Likewise, the chromium-tantalum

steel E23 did not show cutting properties comparable to those of the ordinary high-speed steels. The results of the lathe tests with these steels are summarized in Table 16.

TABLE 16.—*Summary of the lathe tests on some of the steels containing tantalum (+ columbium)*

TESTS WITH SHALLOW CUTS (0.010 INCH DEPTH, 0.0115 IN./REV. FEED, 350 FT./MIN. SPEED)

Steel No.	Chemical composition					Oil quenched from—	Tempered at—	Tests on forging No.	Number of tools tested	Average tool life	Cutting speed for 90-minute tool life [1]
	C	Cr	W	V	Ta (+Cb)						
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	°*F.*	°*F.*			*Minutes*	*Ft./min.*
E97	0.64	3.41	13.02	1.99	------	2,350	1,100	41	8	22.9	305
E23	.69	4.28	------	------	3.45	2,350	650	41	5	0	------
E42	.69	4.23	8.20	1.58	6.05	[3]	[3]	41	------	------	------
E100	1.42	3.37	13.03	.10	1.10	2,350	1,000	41	7	.2	------

HEAVY DUTY TESTS (3/16 INCH DEPTH, 0.028 IN./REV. FEED, 85 FT./MIN. SPEED)

L	0.71	3.60	12.75	1.99	------	2,350	1,100	17	8	11.0	63
E23	.69	4.28	------	------	3.45	2,400	650	17	6	.1	------
E42	.69	4.23	8.20	1.58	6.05	[3]	[3]	17	7	------	------
L	.71	3.60	12.75	1.99	------	2,350	1,100	36	8	[2] 13.9	57
E100	1.42	3.37	13.03	.10	1.10	2,200	1,100	36	8	[2] .5	------
						2,300	1,100	36	8	[2] .5	------
						2,400	1,100	36	8	[2] 3.6	47

[1] Computed from average tool life by means of equation (1) of the text with $n = 1/10$ for shallow cuts and $n = 1/7$ for deep cuts.
[2] Would not harden.
[3] Tests made at 75 feet per minute.

The high carbon, chromium-tungsten-tantalum steel E100 (Table 2) which showed the very large increase in hardness when tempered at 1,100° F. after quenching from high temperatures, failed to show any promise for lathe tools for either shallow cuts or heavy duty. As is shown in Table 16, the tools failed in less than one minute, whereas the high-speed steels of customary composition cut for periods of 10 to 22 minutes under comparable conditions. The best tool life (3.6 minutes) in rough turning was obtained when steel E100 was oil quenched from 2,400° F. and subsequently tempered at 1,100° F.

The four high-speed steels containing 0.6 to 0.9 per cent carbon, in which the 2 per cent vanadium was replaced by different proportions tantalum, gave the best tool performance of any of the steels containing tantalum, but in no case was this as good as the performance of the customary chromium-tungsten-vanadium steel. As is shown in Figure 37, the cutting speeds of the chromium-tungsten-tantalum steels decreased with increase in the proportion of tantalum.

Tantalum does not appear to be promising as a substitute for vanadium or as an alloying element in the customary chromium-tungsten high-speed steels for lathe tools. It acted in a manner similar to aluminum and titanium in that it appeared to decrease

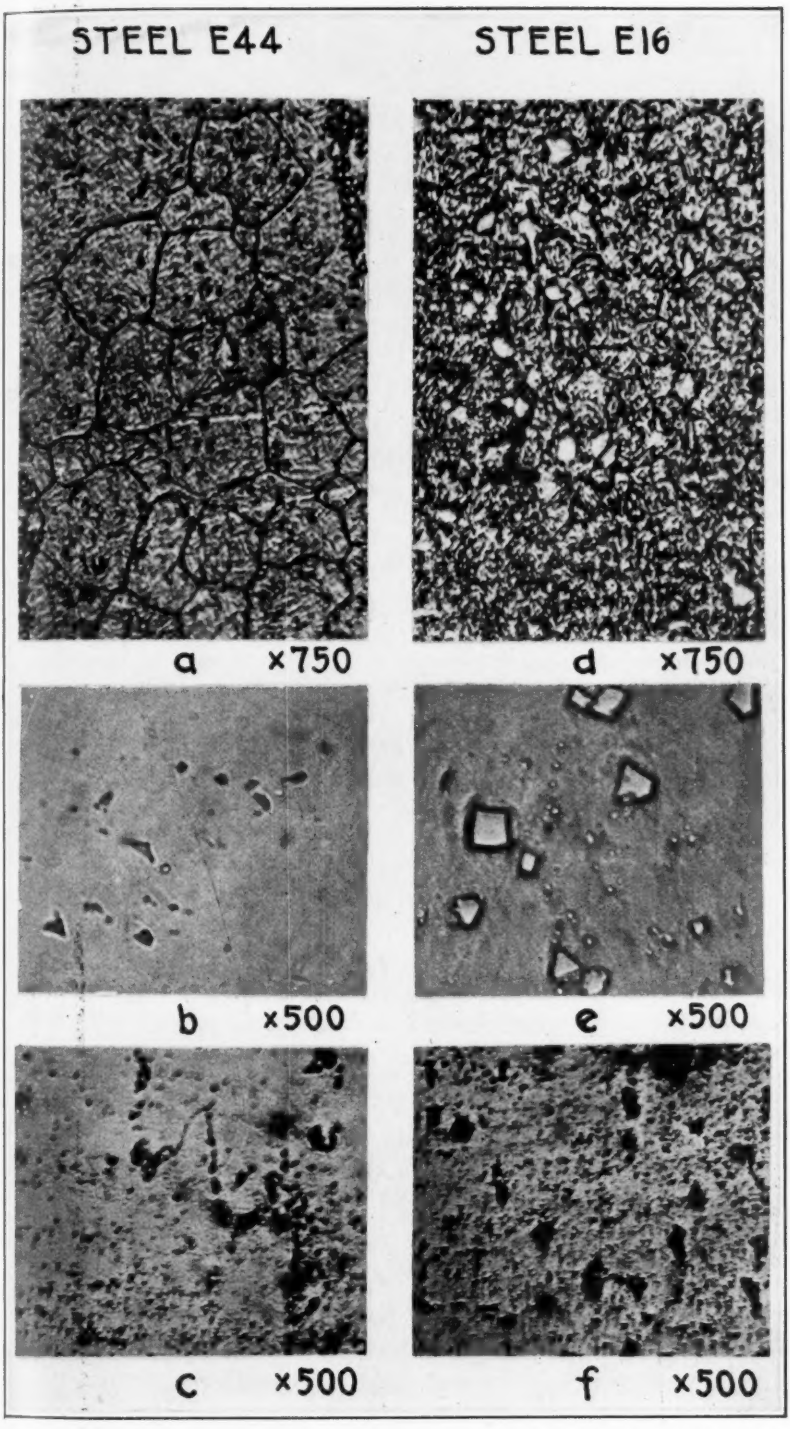

FIGURE 35.—*Structures of two of the chromium-tungsten-tantalum steels as oil quenched from 2,350° F.*

Compositions of the steels are given in Table 2; (*a*) and (*d*), etched with 5 per cent HNO_3 in alcohol; (*b*) and (*e*), unetched; (*c*) and (*f*), etched in boiling solution of $KMnO_4$ (4 g), NaOH (4 g) in 100 ml H_2O.

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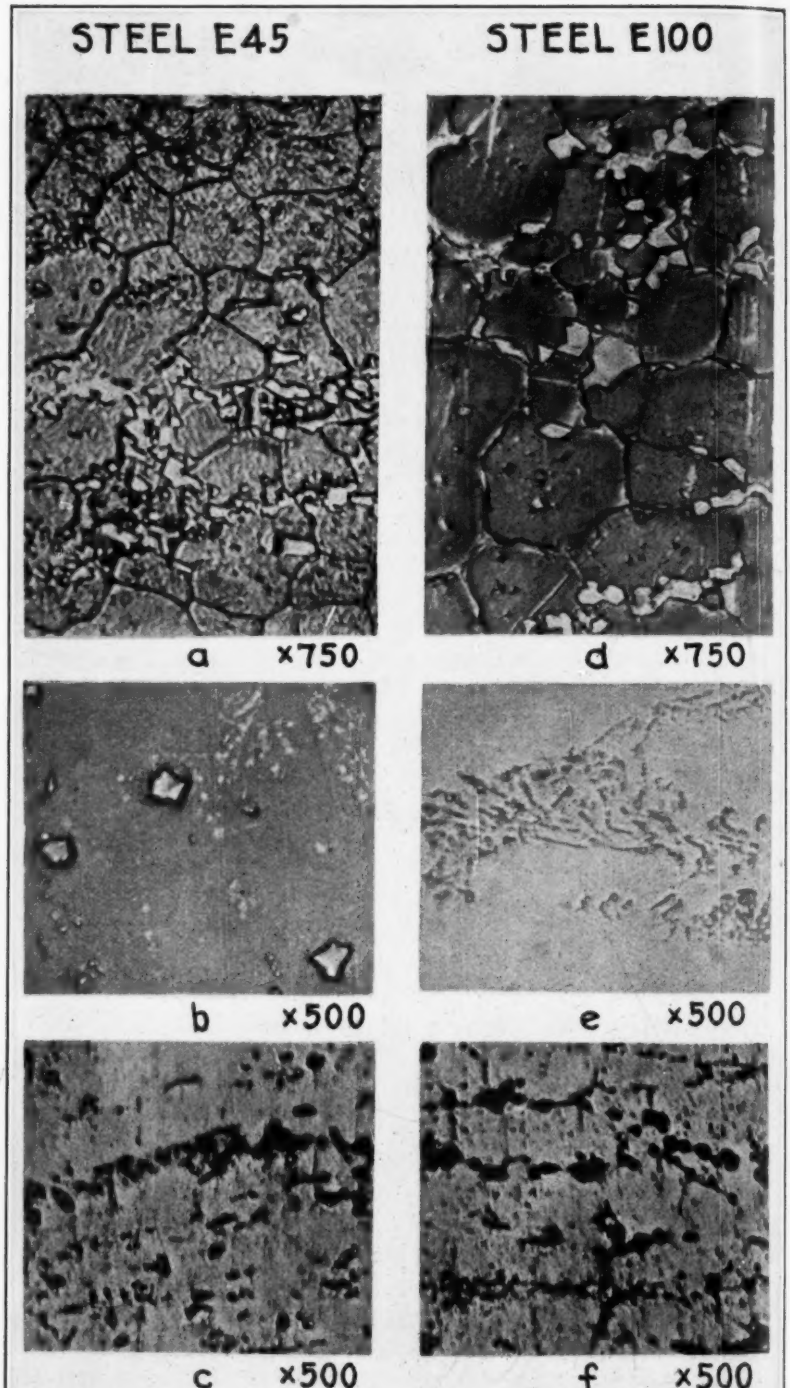

FIGURE 36.—*Structures of two of the high-carbon steels containing chromium, tungsten, and tantalum when oil quenched from 2,350° F.*

Compositions of the steels are given in Table 2; (*a*) and (*d*), etched with 5 per cent HNO_3 in alcohol; (*b*) and (*e*), unetched; (*c*) and (*f*), etched in boiling solution of $KMnO_4$ (4 g), NaOH (4 g) in 100 ml H_2O.

the dissolving power of the austenite for the chromium and tungsten compounds and so decreased the hardness and cutting speeds of the quenched lathe tools.

10. STEELS WITH HIGH PHOSPHORUS OR SULPHUR

Phosphorus and sulphur are present in varying proportions in all commercial steels, and therefore it seemed desirable to determine their effects upon lathe-tool performance in connection with the study of impurities in high-speed steels for shallow cuts, already described. Furthermore, relatively large proportions of phosphorus or sulphur were inadvertently introduced, through one of the lots of ferrovanadium, into some of the high-speed steels containing nickel or cobalt, and it became impracticable to interpret the results of the lathe tests

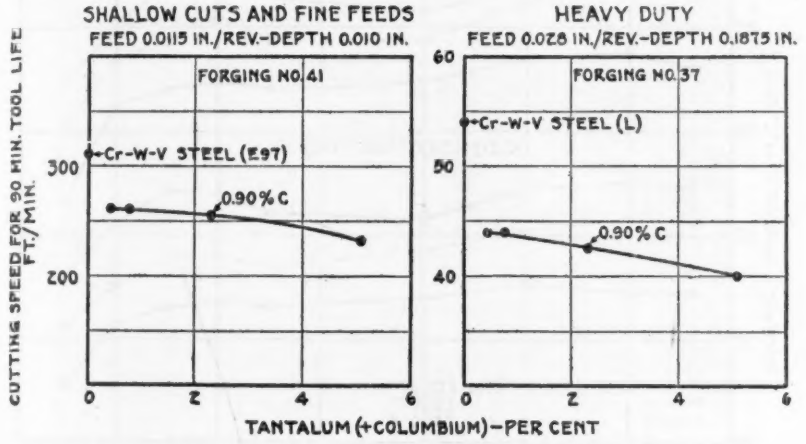

FIGURE 37.—*Effect of tantalum (+columbium) on the cutting speed of high-speed steel tools under shallow cuts and under heavy duty*

Compositions of the tools and their heat treatment are given in Table 2; properties of the forgings are given in Table 3. All tests were made dry.

with these steels without information on the effects of the phosphorus and sulphur present.

As a result of their extended experiments with roughing tools, Taylor and coworkers [50] came to the conclusion—

> that high phosphorus and sulphur are much less injurious to high-speed tools than they were to the carbon tools. However, these elements still exert a somewhat injurious influence upon the steel, and we therefore recommend, inasmuch as the presence of chromium and tungsten in large quantities necessarily render high-speed tools very expensive, that the best qualities of low phosphorus and low sulphur iron should be used in their manufacture.

These views have received the support of a majority of the American manufacturers of high-speed tool steels, as is shown by the results

[50] F. W. Taylor, On the Art of Cutting Metals, Trans. Am. Soc. Mech. Engrs., 28, par. 1087, p. 219; 1907.

of a survey made during 1922 [51] of 66 lots representing 39 commercial brands on the American market. The average proportions of phosphorus and sulphur were 0.023 and 0.027 per cent, respectively, while the ranges were 0.004 to 0.051 per cent phosphorus and 0.009 to 0.061 per cent sulphur.

Comparison of the results in Figure 38 with those for steel E97 in Figure 23 shows that the Rockwell hardness of the high-speed steels was not appreciably affected by 0.058 per cent added phosphorus or 0.215 per cent added sulphur. However, the high-sulphur steels showed a large number of sulphide inclusions (figs. 39 (*a*) and (*b*),

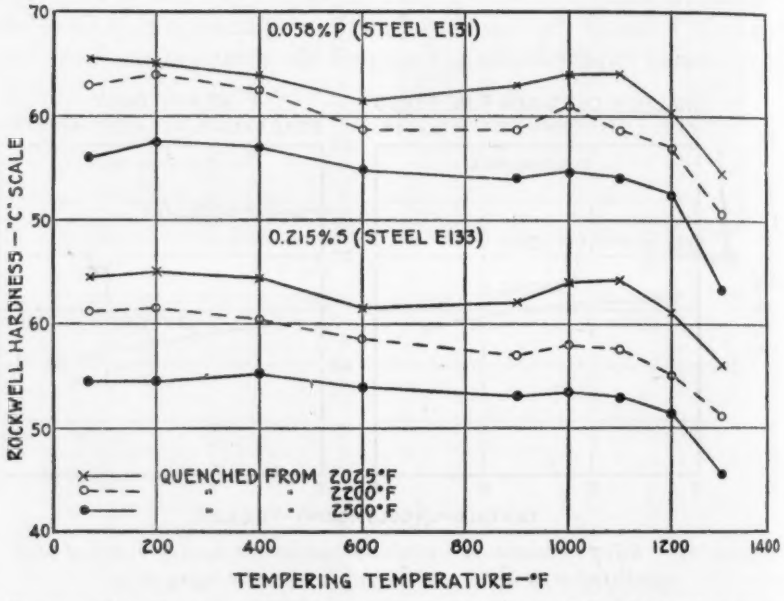

FIGURE 38.—*Hardness of the high-speed steels containing high phosphorus or high sulphur when subjected to different heat treatments*

Compositions of the steels are given in Table 2.

and 40), and there was evidence of phosphide-rich areas in the steel with 0.058 per cent phosphorus (fig. 39 (*c*)).

The sulphide inclusions in the chromium-tungsten-vanadium steels were probably sulphides of both manganese and iron, since the 0.39 per cent manganese in steel E133 is not sufficient to take care of all of the 0.215 per cent sulphur. Similar sulphide inclusions were found in the high-sulphur high-speed steels containing nickel, although they did not have as smooth boundaries as in the steels without nickel and were interspersed with or broken up by white constituents, presumably the carbides and tungstides. It is possible

[51] H. J. French and Jerome Strauss, Lathe Breakdown Tests of Some Modern High-Speed Tool Steels, B. S. Tech. Paper No. 228; 1923.

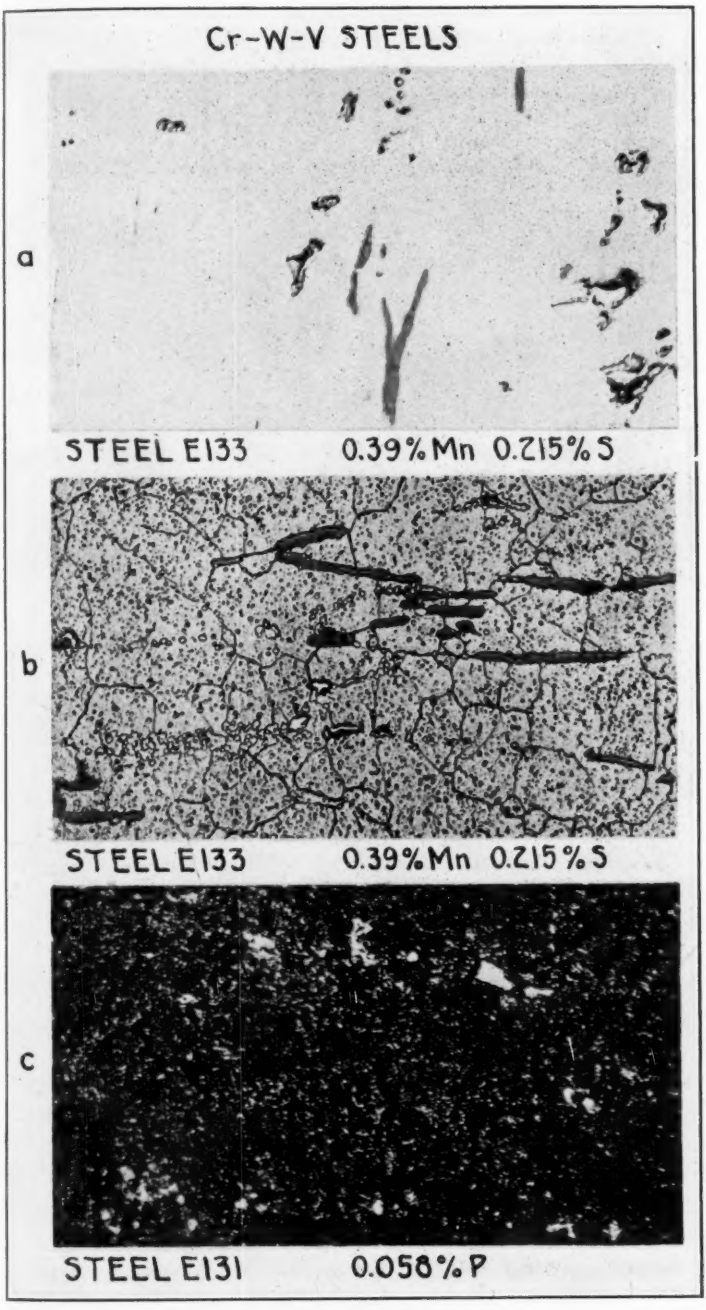

FIGURE 39.—*Structures of hardened high-speed steels containing high phosphorus or high sulphur.* × *500*

Samples oil quenched from 2,350° F., not tempered; (*a*), unetched; (*b*), etched with 5 per cent HNO_3 in alcohol; (*c*), etched with Stead's reagent.

FIGURE 40.—*Structures of hardened high-speed steel containing 3¾ per cent nickel and high phosphorus and sulphur.* × *500*

Samples oil quenched from 2,350° F., not tempered; (*a*), etched with 5 per cent HNO_3 in alcohol; (*b*), etched with 2 per cent HF in water.

that some of the sulphur has combined with the nickel in the high-speed steels containing this latter element, but definite evidence is lacking that this is so, and the significance, if any, of these differences in structural characteristics is not now apparent. The feature of principal interest is that evidence was obtained in the lathe tests that high sulphur was somewhat more detrimental in the high-speed steels with nickel than in those without.

In the lathe tests under heavy duty and also those under shallow cuts (summarized in fig. 41) the steel with 0.058 per cent phosphorus (E131, Table 2) and the steels with 0.135 and 0.215 per cent sulphur showed comparable performance to the steels with much lower proportions of these elements (E129 and E97). Similarly, a cobalt

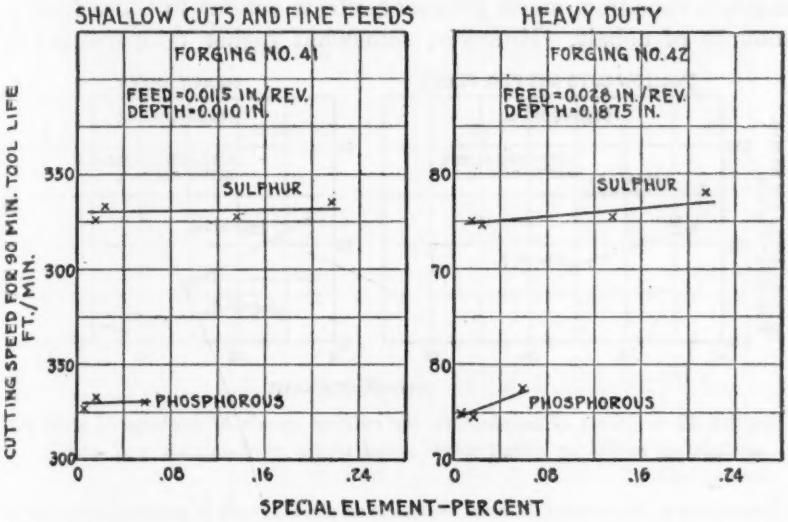

FIGURE 41.—*Effects of phosphorus and sulphur on the cutting speeds of high-speed steel tools under shallow cuts and under heavy duty*

Compositions of the tools and their heat treatments are given in Table 2; properties of the forgings are given in Table 3. All tests were made dry.

high-speed steel with both high phosphorus and high sulphur (E15) had a cutting speed equal to that of a similar steel with low phosphorus and sulphur (steel A, Table 2). On the other hand, the nickel-bearing high-speed steel with 0.057 per cent phosphorus and 0.125 per cent sulphur, had a lower cutting speed than a similar steel with about 0.02 per cent of each of these elements.

It may, therefore, be said that phosphorus up to about 0.06 per cent and sulphur up to 0.215 per cent do not appear to be injurious, from the viewpoint of lathe tool performance, when present individually or together, in the customary chromium-tungsten-vanadium steels, with or without cobalt. However, high sulphur tended to lower the cutting speeds in the presence of nickel.

Because of the possibility of segregation of the phosphorus and the introduction of numerous sulphide inclusions in high-sulphur steels these two elements may react disadvantageously by promoting lack of uniformity and localized weaknesses. Therefore, they can advisably be kept within low limits for all high-speed steel lathe tools.

11. STEELS WITH NICKEL

The close proximity of nickel and cobalt in the periodic system of the elements and recognition of the benefits derived from cobalt has frequently raised the question of substituting nickel for cobalt in high-speed tool steels.

Previously reported tests with roughing tools [52] showed that the addition of about 3¾ per cent of nickel to the customary chromium-tungsten-vanadium steels produced effects similar to those from like amounts of cobalt. However, somewhat higher temperatures had

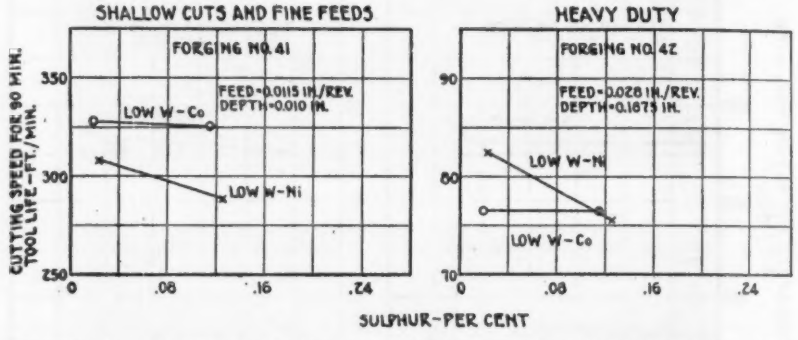

FIGURE 42.—*Effects of sulphur on the cutting speeds of high-speed steel tools containing nickel or cobalt when tested under shallow cuts and also under heavy duty*

Compositions of the tools and their heat treatments are given in Table 2; properties of the forgings are given in Table 3. All tests were made dry.

to be used in hardening the nickel steels than in the steels without nickel to produce the best tool performance, and in this respect nickel and cobalt acted similarly. On the other hand, it was more difficult to put the high-speed steels with nickel into a machinable condition than it was with steels containing cobalt or steels without nickel or cobalt, unless an adjustment was made in the carbon content. With decrease in carbon from 0.6 or 0.7 to 0.5 per cent, the steels with nickel could themselves be readily machined while the tool performance under heavy duty remained substantially the same.

These tests were all made under heavy duty, and two of the nickel steels contained high phosphorus or sulphur, or both. For this reason the rough turning tests were repeated on steels containing low proportions of phosphorus and sulphur, and the results are included in Table 17 with those obtained under shallow cuts and fine feeds.

[52] H. J. French and T. G. Digges, Experiments with Nickel, Tantalum, Cobalt, and Molybdenum in High-Speed Steels, Trans. Am. Soc. Steel Treat., 8, p. 861; 1925.

TABLE 17.—*Lathe tool performance of high-speed steels with and without nickel*

Steel No.	Chemical composition							Oil quenched from—[1]	Cutting conditions				Number of tools tested	Average tool life	Cutting speed for 90-minute tool life[2]
	C	Cr	W	V	P	S	Ni		Forging No.	Speed	Feed	Depth of cut			
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*° F.*		*Ft./min.*	*In./rev.*	*Inch*		*Minutes*	*Ft./min.*
TESTS UNDER HEAVY DUTY															
E129	0.63	3.94	13.03	2.00	0.017	0.023		2,350	42	100	0.028	3/16	5	11.4	74.5
E97	.64	3.41	13.02	1.99	.006	.015		2,350	42	100	.028	3/16	5	12	75
E130	.61	3.94	13.03	1.90	.017	.023	3.81	2,350	42	100	.028	3/16	5	17.5	79
								2,400	42	100	.028	3/16	5	22.9	82.5
E14	.69	3.64	13.75	1.92	.057	.125	3.70	2,350	42	100	.028	3/16	5	8.9	72
								2,400	42	100	.028	3/16	5	12.3	75.5
L	.71	3.60	12.75	1.99	.029	.026		2,350	18	85	.028	3/16	8	11	63
E14	.69	3.64	13.75	1.92	.057	.125	3.70	2,400	18	85	.028	3/16	6	11.4	63.5
E41	.51	3.85	12.72	1.95	.019	.020	3.54	2,400	18	85	.028	3/16	6	12.5	64.5
TESTS UNDER SHALLOW CUTS															
E129	0.63	3.94	13.03	2.00	0.017	0.023		2,350	41	380	0.0115	0.010	6	23.7	333
E97	.64	3.41	13.02	1.99	.006	.015		2,350	41	380	.0115	.010	6	19.2	326
E130	.61	3.94	13.03	1.90	.017	.023	3.81	2,350	41	380	.0115	.010	6	6.8	294
								2,400	41	380	.0115	.010	6	11	308
E14	.69	3.64	13.75	1.92	.057	.125	3.70	2,350	41	380	.0115	.010	6	6.8	294
								2,400	41	380	.0115	.010	6	5.5	288
E97	.64	3.41	13.02	1.99	.006	.015		2,350	41	380	.0115	.010	8	22.8	332
E41	.51	3.85	12.72	1.95	.019	.020	3.54	2,400	41	380	.0115	.010	8	5.6	288
E97	.64	3.41	13.02	1.99	.006	.015		2,350	41	380	.0115	.010	8	16.4	321
E14	.69	3.64	13.75	1.92	.057	.125	3.70	2,400	41	380	.0115	.010	8	5.5	288
E108	.66	3.90	18.25	1.12	.027	.012		2,400	41	380	.0115	.010	7	17.8	324
E22	.61	3.66	17.40	1.02	.043	.073	3.71	2,450	41	380	.0115	.010	7	5.2	287
E97	.64	3.41	13.02	1.99	.006	.015		2,350	41	400	.0115	.005	6	14.6	334
E22	.61	3.66	17.40	1.02	.043	.073	3.71	2,450	41	400	.0115	.005	6	7.6	313

[1] All tools annealed at 1,600 to 1,650° F.; tempered 30 to 45 minutes at 1,100° F. after hardening.

[2] Computed from equation (1) of the text with $n = \frac{1}{7}$ for deep cuts and $n = \frac{1}{10}$ for shallow cuts.

NOTE.—All tests made dry with tools of the form shown in Figure 5. The tests in each block constitute a complete run at one time in sequence at different diameters of the test forgings.

The results in Table 17 show that the addition of 3¾ per cent of nickel to the customary chromium-tungsten-vanadium steels was beneficial for the rough turning tools but detrimental to the tools used under shallow cuts and fine feeds.

In the rough turning tools the addition of nickel, together with a 50° F. increase in the quenching temperature, produced an appreciable improvement in the performance of the high-speed steels, but the same tools were not as good under shallow cuts as the tools free from nickel which were hardened at lower temperatures.

The fact already mentioned that the high-speed steels with nickel could not themselves be readily machined, even after prolonged annealing, suggested lowering the carbon content from around 0.6 or 0.7 to 0.5 per cent. This did not affect the performance of the roughing tools appreciably, as is shown in Table 17, but was detrimental in the tools used under shallow cuts.

XII. SUMMARY AND CONCLUSIONS

1. A method is described for testing lathe tools under shallow cuts and fine feeds. It is based upon the fact that when two tools are set at equal depths in one tool holder the second or "trailing" tool will not cut so long as the "leader" or cutting tool shows no wear. With the carbon and high-speed steel tools used, the second tool began to cut when the leader had worn 0.001 to 0.002 inch, and at this point the leader or test tool was considered to have failed. All subsequent comments on turning with shallow cuts and fine feeds are based on this end point, but greater wear can be made to represent tool failure by using a shallower setting for the second tool than for the cutting tool.

2. Tests were made dry at different cutting speeds, feeds, and depths of cut on nickel steel forgings with tensile strengths of 80,000 to 100,000 lbs./in.^{2} to give a broad background for the interpretation of the results of tests of different tool steels, first heat treated in various ways. The results could be represented approximately by the following equations, in which V is the cutting speed, T the tool life, F the feed, D the depth of cut, A the area of cut ($=DF$), c, K, K_1, K_2, and n are constants.

For high-speed steel tools

$$VT^{\frac{1}{n}}=c \tag{1}$$

$$V=K_1-K_2\ (DF)=K_1-K_2A \tag{2}$$

For carbon steel tools

$$V=\frac{K}{DF}=\frac{K}{A} \tag{3}$$

These equations are not to be construed to represent the true laws of cutting, since the cutting speed is probably not affected equally by

variations in the feed and the depth of cut. However, they represent approximately the results of the experiments made with the depths of cut of 0.005 to 0.020 inch and feeds of 0.0115 to 0.0204 in./rev.

3. In the tests of short duration, where tool failure occurred in about 2 to 10 minutes, the tool life was increased somewhat more by the use of water than by lard oil, but in tests of about 50 minutes duration, under the same feed and depth of cut but lower cutting speeds, these two liquids produced effects of the same magnitude. The increases in tool life from the use of these liquids were not large in any case, but the finish on the work piece at the end of the cut was better with the liquids than without.

4. Tests with tools of different forms and angles showed that the successful application of the described method of test was not dependent upon having the broad-nose tool used in a majority of the experiments. Tools with a plan angle of 65° had a longer life than the broad-nose tools, but the finish produced on the nickel steels in dry turning did not appear to be as good. The best tool life with the broad-nose tools was obtained with a back slope of 30°; a side slope of 0° was better than 8°.

5. The cutting speed of quenched carbon steel tools was not affected appreciably by variations in carbon content from 0.75 to 1.3 per cent nor by subsequent tempering at temperatures up to 375° F., which did not lower the hardness; the cutting speed of the carbon steel tools was equal approximately to that of a quenched "oil hardening" tool steel and only slightly lower than the cutting speed of a steel containing 1.3 per cent carbon and 2¾ per cent tungsten.

6. The cutting speed of carbon steel tools was lower in all cases than that of high-speed steel tools, but the differences between the two decreased with decrease in the areas of cut in dry turning.

7. The heat treatments which resulted in the best roughing tool performance for high-speed steels of customary compositions also resulted in superior performance under shallow cuts and fine feeds. These treatments comprised oil quenching from the highest practical temperatures followed by tempering to convert the larger part of the retained austenite to martensite.

8. Of 12 elements added in different proportions to chromium-tungsten or chromium-tungsten-vanadium high-speed steels only one—cobalt—produced decidedly beneficial results. Molybdenum and nickel offered promise under certain conditions, while the remainder either had a negligible effect or were definitely deleterious from one viewpoint or another.

9. Cobalt improved the performance of the high-speed steel tools both under shallow cuts and under heavy duty, but the maximum benefits were obtained only with high hardening temperatures. The percentage gain from the addition of cobalt was somewhat greater

in rough turning than with shallow cuts and fine feeds, but increase in cobalt above about 5 per cent did not produce improvements commensurate with those resulting from 3.5 to 5 per cent and high hardening temperatures.

10. Replacement of part or all of the tungsten in high-speed steels by molybdenum, in the ratio of 1 part molybdenum to 2½ parts of tungsten, produced steels having performance comparable to that of the tungsten steels. Such substitution should be useful in case of a depleted tungsten supply but is not advocated at the present time, since there was some evidence of irregular performance in the high molybdenum steels, and their hot working properties did not seem to be as good as those of the tungsten steels. However, a steel with 7 per cent molybdenum and no tungsten had one advantage over the tungsten steels for roughing tools in that its hardness and performance were not so largely affected by variations in the hardening temperatures.

11. The addition of 3¾ per cent of nickel to the customary chromium-tungsten-vanadium steels was beneficial for the rough turning tools, particularly when combined with a 50° F. increase in the hardening temperatures, but was detrimental to the tools used under shallow cuts and fine feeds and adversely affected the machining properties of the high-speed steel itself. Lowering the carbon from 0.6 or 0.7 to 0.5 per cent improved the machining properties without affecting the performance of the roughing tools but was detrimental to the tools used under shallow cuts.

12. Each of the four elements—arsenic, antimony, copper, and tin—adversely affected the tool performance of high-speed steels under shallow cuts, and the magnitude of the decrease became greater as the proportions of these elements increased. Copper was the least harmful; next in order came tin, while arsenic and antimony were the most objectionable.

13. The effects of these four elements upon the performance of roughing tools did not necessarily correspond to those observed with shallow cuts. The 0.8 per cent arsenic addition lowered the cutting speed, but the addition of 0.4 per cent antimony or 0.5 per cent or less of tin had no measurable effect. Higher proportions of tin lowered the cutting speeds. The high-speed steels containing 0.36 to 1.77 per cent copper showed slightly better performance than the corresponding steels without copper.

14. The steels containing 0.4 per cent antimony, 0.8 per cent or more of copper, or 0.8 per cent arsenic did not have good hot working properties, (illustrated by numerous corner cracks on the bars), while those containing 1.7 per cent antimony or 1.8 per cent tin showed a high degree of hot shortness and could not be forged or rolled. Also,

the steel with 1.77 per cent copper could itself be machined only with difficulty in the annealed condition.

15. Phosphorus up to about 0.06 per cent and sulphur up to 0.215 per cent did not appear to be injurious, from the viewpoint of lathe-tool performance of the customary chronium-tungsten-vanadium steels, with or without cobalt. However, high sulphur tended to lower the cutting speeds in the presence of 3¾ per cent nickel. Because of the possibility of segregation of the phosphorus and the introduction of numerous sulphide inclusions in high-sulphur steels these two elements can advisedly be kept within low limits for all high-speed steel lathe tools.

16. Aluminum adversely affected the performance of the high-speed steel tools both with shallow cuts and under heavy duty. It was one of the few metals considered which, in proportions around 0.3 per cent, produced a measurable decrease in the cutting speeds in rough turning. This decrease became greater as the proportion of the aluminum was increased, and with 0.8 per cent the drop in cutting speed was greater than that produced by equal proportions of any of the other elements considered. These changes were accompanied by decrease in the hardness of the quenched steels probably through decrease in the dissolving capacity of the aluminum-iron solid solution for carbon, chromium, tungsten, and vanadium. With 0.8 per cent aluminum there was also evidence of a low melting eutectic in samples quenched from 2,350° F.

17. Titanium was another of the elements which appeared to lower the dissolving capacity of the austenite, and as a result the hardness and the cutting speeds of the high-speed steel tools decreased with increase in the titanium. Its interference was lessened, probably through the formation of less harmful carbides, instead of solution as titanium in the austenite, by increasing the carbon content of the steel.

18. Tantalum did not appear to be promising as a substitute for vanadium or as an alloying element in the customary chromium-tungsten high-speed steels for lathe tools. It acted in a manner similar to aluminum and titanium in that it appeared to decrease the dissolving power of the austenite for the chromium and tungsten compounds and so decreased the hardness and cutting speeds of the quenched lathe tools.

XIII. ACKNOWLEDGMENTS

Acknowledgments are due to a number of the authors' associates as follows: To C. F. Raab, machinist, whose care in grinding all of the tools and help in carrying out many of the lathe tests contributed appreciably to the consistent results obtained; to W. V. Magruder,

laboratory aid, for carrying out many of the heat treatments, hardness, and lathe tool tests; to H. K. Herschman, associate metallurgist, and S. J. Rosenberg, assistant metallurgist, for the preparation of the micrographs; and to H. Bright, associate chemist, for the chemical analysis of the tools.

WASHINGTON, April 12, 1929.

FURTHER EXPERIMENTAL PRODUCTION OF CURRENCY PAPER IN THE BUREAU OF STANDARDS PAPER MILL[1]

By Merle B. Shaw and George W. Bicking

ABSTRACT

The work continues the investigation to improve the durability of United States currency paper previously reported in Technologic Paper No. 329. The wear-resistant quality of currency paper was very much increased as a result of the experimental tests described in the earlier publication, but additional study of the paper-manufacturing processes with a view to further prolonging the service life of the currency was subsequently requested. The research was conducted in cooperation with the Bureau of Efficiency and the Bureau of Engraving and Printing.

The study included the use of caustic soda as compared with lime for cooking the rags, the effect of variation in the fiber composition of the paper, the effect of modifications in the beating process, determination of optimum surface-sizing conditions for best printing results, and printing tests on the finished experimental papers.

The data showed that either lime or caustic soda is satisfactory as the digesting agent in the cooking process. Fiber mixtures of 75 per cent linen and 25 per cent cotton gave the best paper for currency use, although paper made from equal proportions of these fibers was of very good quality. Gradual application of roll pressure in the beating process was found to be essential to best results. Formaldehyde proved better than alum as glue preservative in the surface-sizing bath.

Comparative tests of commercial manufacturing procedure and bureau practice were made at the request of manufacturers desiring to produce paper of the type developed in the investigation. The experimental procedure gave equally good results with commercial equipment, and paper of similar quality is now being made commercially.

Description of the manufacturing procedure, tables of experimental data, and discussion of the results are included in the publication.

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[1] Supplemental to B. S. Tech. Paper No. 329.

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I. INTRODUCTION AND RÉSUMÉ OF PREVIOUS WORK

Results of research on the production of currency paper in the Bureau of Standards experimental paper mill were published previously in Technologic Paper No. 329,[2] issued October, 1926. The present publication relates to a continuation of the study and is supplementary to the earlier work.

The previous publication dealt with various proportions of linen and cotton paper-making fibers and a study of the paper-making processes. Lime was the cooking chemical employed in the pulping operation. Conclusions as to the fiber composition and the paper-making procedure found to yield the most satisfactory paper were included in the publication.

The paper produced in the experimental tests was of good printing quality and of much greater strength than that in use when the investigation was initiated. The experimental procedure was applied in commercial production with such satisfactory results that the Treasury Department consequently revised the contract specifications. Currency paper of more than double the strength previously specified was subsequently delivered, without increase in cost to the Government or to the manufacturing contractor. Statistics of the Treasury Department show that as a result of the research the average service life of paper currency was increased about 40 per cent.

The principal factor in the improvement of the durability of the paper was the manner and duration of the beating treatment accorded the fibers in the manufacturing process. Full details of the beating

[2] Publication may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C. Price, 10 cents.

procedure developed and recommended were included in Technologic Paper No. 329.

There seems to have been no demand previously for commercial paper of such high fiber strength as that made experimentally at the bureau in the investigation. Since the completion of the work described in the earlier publication, however, a number of fine-paper manufacturers have become interested in its production and have cooperated with the bureau in the later investigative work to develop this type of paper for various commercial uses. The results reported in this and in the previous paper are considered, therefore, to be of value in the manufacture of fine rag papers in general, as the processes developed appear to be applicable to several types of commercial papers, particularly bonds and ledgers.

The present report gives the results of comparative study of commercial manufacturing operations and bureau practice; further experimental study of the beating procedure with the fiber mixture specified for currency paper; the use of other combinations of these fibers; the use of caustic soda, as compared with lime, for cooking the rags; and tests to establish the best procedure for surface-sizing the paper-machine product.

Since the methods and theoretical considerations were, to a large extent, the same as those described in the preceding publication, the present article will be limited, in general, to the essential respects in which the work deviated from that described before, and to a statement of the results obtained.

II. PAPER-MAKING FIBER USED

It was not considered expedient when starting the investigation to outline the complete program, and, consequently, the raw materials were not all purchased at one time. Those secured for the present tests, however, duplicated as nearly as possible the earlier purchases and, like those, also were obtained from the stock used by a manufacturer of the Government currency paper. The materials consisted of new rags graded as white and cream linen cuttings, brown and gray linen cuttings, white cotton shirt cuttings, and cream cotton hosiery clippings. The composition of the beater "furnish"—that is, the various paper-making materials blended in the beater—is included in the description of each paper-machine run.

III. PAPER-MAKING EQUIPMENT

The paper mill of the bureau is equipped for making paper on a semicommercial scale under practical mill conditions. The equipment employed in the manufacture of experimental currency paper was that in general use in the mill and consisted of a rag duster; rag

cutter; rotary boiler; 50-pound copper-lined wood-tub beater, having manganese-bronze bars and plate and equipped with a washing cylinder; 300-pound tile-lined cement beater, having phosphor-bronze bars and plate and equipped with two washing cylinders; small Jordan refiner with iron bars; a 4-plate screen; a 29-inch Fourdrinier paper-making machine, with wire 33 feet long and having two presses, nine 15-inch dryers, a small machine stack of seven rolls, and a reel; a surface-sizing bath and drying cabinet; and a 5-roll supercalender.

Photographs of the duster, cutter, rotary boiler, 50-pound beater, Jordan, and Fourdrinier machine are shown in B. S. Technologic Paper No. 340, Caroá Fiber as a Paper-Making Material, pages 338 to 341. Photographs of the surface-sizing equipment follow herein.

IV. PREPARATION OF THE HALF STUFF

The procedure followed in the preparation of the half stuff was essentially the same as that generally observed in the commercial production of high-grade papers.

1. CLEANING AND CUTTING

Since the rags employed in the tests were new and already graded as to material and color (uniform in quality), only dusting, cutting, and subsequently dusting again were necessary to prepare the material for the digestion process. In the cutting operation the rags were reduced to pieces averaging less than 10 square inches in area.

2. COOKING

The cooking process, which dissolves the noncellulose material and softens the paper-making fiber, thereby permitting it to respond more readily to the subsequent treatment, freed the rags from such impurities as dyes, size, starch, dirt, grease, or other incrusting materials. In the work previously reported lime was used in the boiling solutions, but in the tests described in this paper caustic soda and lime each served as a solvent to effect the chemical cleansing.

The constant factors for each cook, whether lime or caustic soda was used, were as follows:

Weight of bone-dry fiber	pounds	106
Volume of water	gallons	52.5
Initial temperature	° F.	70–80
Duration of initial temperature	hour	1
Time for raising to cooking temperature	do	1
Cooking temperature	° F.	250–260
Duration of cooking temperature	hours	5
Cooking pressure	pounds	30–40

Unless otherwise stated the white and cream linens were kept separate from the gray and brown in cooking, and the cotton rags were cooked alone. The few departures from this procedure are specifically noted in the description of the corresponding paper-machine run.

The strength of the cooking liquor was varied according to the kind of rags being treated. In the case of lime cooks, 6 per cent of lime, based on the weight of the rags, was used for the cotton and the white and cream linens; 12 per cent for the colored linens. For the soda process 2 per cent of commercial caustic soda (96 per cent sodium hydroxide) was employed for the cotton rags (light-colored); 4 per cent for the light-colored linens; and 5 per cent for the dark-colored linens. In the few cases in which light and dark linens were cooked together, 4 per cent of caustic soda was used when the mixture was 25 per cent cotton and 75 per cent linen; 3 per cent when 50 per cent cotton and 50 per cent linen. The amounts of caustic used were not predetermined by experimental tests but were selected on judgment. They proved very satisfactory, however, and, as shown by the tests, were very close to the quantities required.

In preparing the lime solution a small amount of the water was used for slaking, and the remainder of the 52.5 gallons was later added to and thoroughly mixed with the slaked lime. The mixture was run into the boiler through a 60-mesh screen to remove sand, splinters of wood, coal particles, or other objectionable material. The caustic soda was dissolved in the water, which was equal in volume to that used for the lime cook, and the solution likewise screened as it was charged into the boiler.

3. WASHING

The cooked rags were transferred to the 50-pound beater and washed until the effluent was clear, to remove the cooking liquor and the loosened impurities. One-half of a cook constituted a charge. The time required for washing was about two and one-half hours. The amount of water used was 1,500 gallons, or 30 gallons per pound of rags, for each complete operation.

The beating action was continued further to brush the fibers out of weave. The cotton and uncolored linens responded somewhat more readily to this treatment than the gray or brown linens. The former materials required from 6½ to 7 hours, and the latter, 7 to 7½ hours, for conversion into the partially prepared pulp, commonly termed "half stuff."

4. BLEACHING

A solution of calcium hypochlorite, from bleaching powder, was mixed with the half stuff, which was then dropped into a drainer where the liquor was allowed to drain off and the residual bleach to become spent. The procedure followed was, in general, the same as that

described in Technologic Paper No. 329, pages 95 and 96. Any deviation therefrom is noted in the description of the corresponding paper-machine run.

5. LOSS OF FIBER

The loss of fiber sustained in converting the rags to half stuff was determined for a few of the cooks by the caustic-soda process.

The total loss in cooking, washing, and bleaching mixtures of 75 per cent linen and 25 per cent cotton rags, cooked together, with 4 per cent of caustic soda, was from 15 to 19 per cent. The determination was made for each of three cooks. For a boiler furnish of 50 per cent linen and 50 per cent cotton, cooked with 3 per cent of caustic, the total loss was 13.75 per cent. For 100 per cent cotton, cooked with 2 per cent of caustic soda, the total loss was 7 per cent, but in the case of 100 per cent linen, cooked with 4 per cent of caustic soda, the loss was 21 per cent.

V. PAPER-MAKING PROCESSES

1. BEATING

The beating was conducted in the same manner as described in Technologic Paper No. 329. The characteristic feature of the method of beating used at the bureau in the production of experimental currency paper is the very gradual lowering of the beater roll.

Before the furnish was added to the beater the roll was raised off the plate, by turning the handwheel, in order to give clearance to the lumps of half stuff. The tub was partially filled with water, half stuff from the drainers was introduced, and additional water was run in until the desired concentration was obtained. After sufficient circulation of the furnish the roll was gradually lowered on the plate, by definite amounts and at fixed intervals, to brush out the fibers and reduce them to optimum length.

Measurements were made indicating the relative rate at which water drained from the stuff. Since the fibers differed by nature, however, in physical characteristics and resultant susceptibility to the hydrating influence of the beating action, the beating was controlled by manipulation of the roll, and was independent of the results of the freeness tests. The duration of the beating and the observed freeness readings are recorded for the machine runs in Table 1.

For further details of beater manipulation and discussion of the factors affecting the freeness of the beaten pulp, and the consequent characteristics of finished paper, the reader is referred to the earlier publication, pages 96 to 102. Description of the apparatus and method used in measuring the freeness of the stuff are also included.

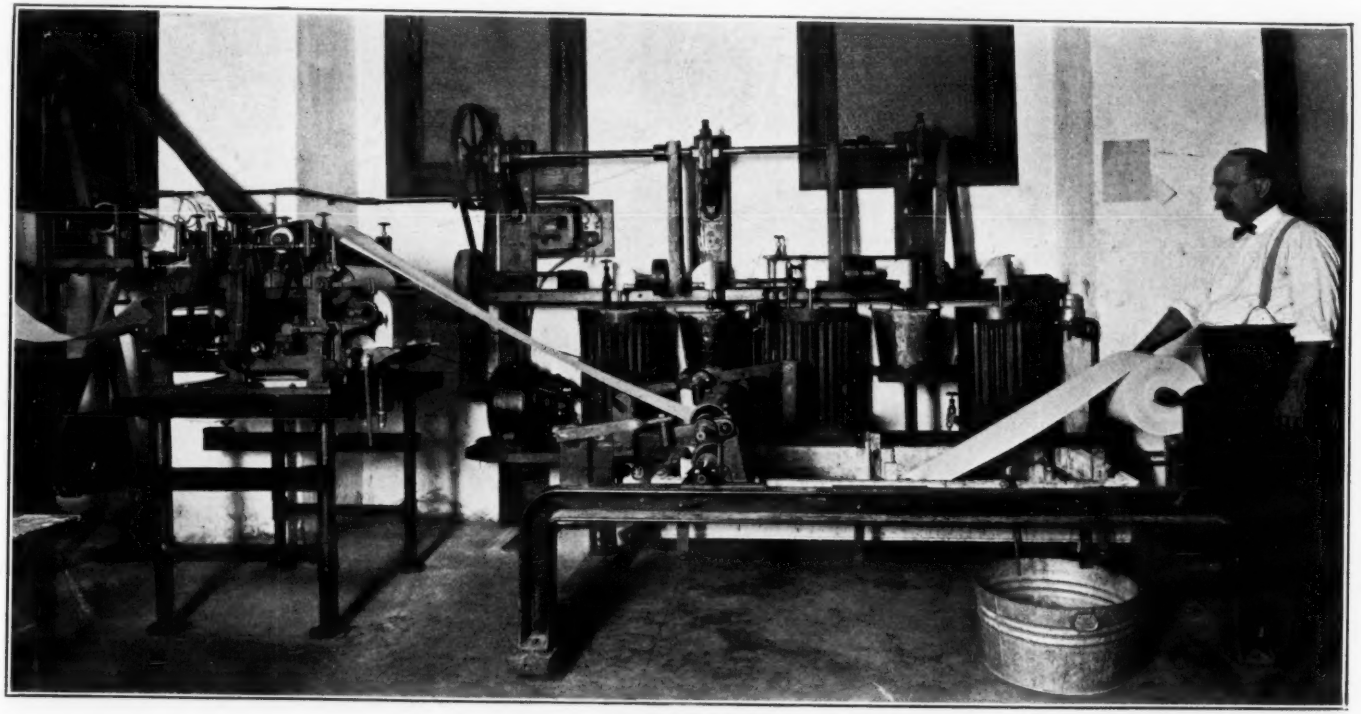

FIGURE 1.—*Surface-sizing vat*

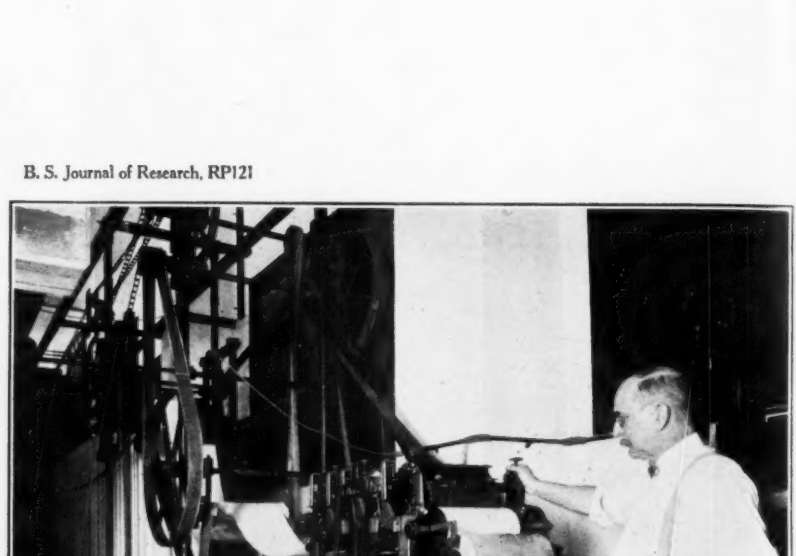

FIGURE 2.—*Festoon rack*

(Coating machine in foreground not used in currency tests.)

2. PAPER-MACHINE OPERATION

From the stuff chest the beaten half stuff was pumped in a continuous stream through the stuff box and the Jordan refiner, and thence to the paper machine. Pumping the stock from the Jordan directly to the paper machine is considered better practice than discharging it into a machine chest and subsequently withdrawing it as needed. By the former method changes in the character of the stock indicated as desirable by conditions at the screen, on the paper machine, or in the finished sheet can be effected rapidly by suitable adjustments of the Jordan.

The operation of the paper machine was very carefully controlled during the tests. For additional details of the operation see Technologic Paper No. 329, pages 102–103.

3. GLUE SURFACE SIZING

Some of the papers were surface sized for experimental printing tests. The waterleaf or unsized paper thus treated was run through a heated solution of animal glue, passed between a pair of squeeze rolls which removed the excess size, and hung in festoons to dry. The final operation consisted in passing the dried paper through the supercalender to give it the desired finish.

Figures 1 and 2 show the surface-sizing equipment. The vat for the sizing solution is an open wooden box, 58½ by 24 by 8 inches. It is heated by a steam coil of three-fourths inch galvanized-iron pipe 20 feet in length, and contains three adjustable rolls for regulating the degree of immersion of the paper in the bath. The squeeze rolls are 5 inches in diameter. The upper roll is brass and the lower one has a rubber covering on a steel core. The festoon rack is 15 feet long and has a capacity of 28 loops, each 6 feet in length. With the uptake rack and the rack from the festoons to the reel, the capacity of the dryer is 400 feet. The dryer is inclosed in a cabinet equipped for air conditioning and temperature control. The view shows the festoon system without the cabinet.

The sizing solutions employed in the tests contained from 1 to 6 per cent of glue, and alum or formaldehyde added as a preservative. The temperature ranged from 120° to 140° F. Description of the tests is included in the section, Glue Surface-Sizing Tests, following.

VI. TEST DATA ON FINISHED UNSIZED PAPER

Table 1 gives data relative to the furnish and the operation of the beater for each machine run, and various measurements on the finished waterleaf or unsized paper. The apparatus and methods em-

ployed in making the measurements, with the exception of copper number, are fully described in Paper Testing Methods, published by the Technical Association of the Pulp and Paper Industry, 18 East Forty-first Street, New York, N. Y. The method used to determine copper number is described in Bureau of Standards Technologic Paper No. 354.[3]

[3] A Modified Method for Determination of the Copper Number of Paper, by B. W. Scribner and W. R. Brode. (B. S. Tech. Paper No. 354.) Superintendent of Documents, Government Printing Office, Washington, D. C. Price, 5 cents.

TABLE 1.—*Data on unsized papers*

TABLE 1.—*Data on unsized papers*

A. TESTS WHOLLY AT BUREAU OF STANDARDS

Machine run No.	Chemical used in cooking	Fiber composition		Beating interval	Freeness of stock		Physical tests												Chemical test, copper No.
		Linen	Cotton		After beating	At head box	Weight, 25 by 40 inches, 500 sheets	Bursting strength	Ratio of bursting strength to weight, 25 by 40, 500 sheets	Thickness	Folding endurance		Tensile strength (strip 15 by 100 mm)		Elongation		Tearing strength		Opacity	Gloss	
											Machine direction	Across machine direction	Machine direction	Across machine direction	Machine direction	Across machine direction	Machine direction	Across machine direction			
		Per cent	*Per cent*	*Hr. Min.*			*Pounds*	*Points*	*Per cent*	*Inch*	*Double folds*	*Double folds*	*kg*	*kg*	*Per cent*	*Per cent*	*g*	*g*		*Per cent*	
658	Lime	75	25	16 30	36	------	61.5	45.6	74.1	0.0039	6,755	4,485	10.49	5.56	3.7	9.2	133.2	122.4	0.863	29.0	0.483
659	do	75	25	16 00	35	------	59.8	46.1	77.1	.0039	6,565	5,250	9.54	5.46	1.4	5.9	146.8	148.0	.868	29.0	.618
660	do	75	25	12 00	32	------	60.0	45.1	75.2	.0039	5,465	5,090	9.75	5.62	3.5	8.7	139.2	132.0	.891	28.0	.574
661	do	75	25	14 00	35	------	59.8	44.8	74.9	.0038	4,960	4,625	9.84	5.47	3.5	9.3	143.6	130.0	.807	30.0	.898
668	do	75	25	12 00	47	------	57.4	42.0	73.2	.0038	5,840	4,385	9.25	5.23	3.3	7.6	150.4	141.2	.819	31.2	.649
670	do	75	25	13 00	35	------	62.1	44.5	71.6	.0041	5,335	5,530	9.95	5.61	3.8	9.1	148.4	148.4	.838	30.0	.640
671	do	50	50	13 00	37	------	60.0	45.0	75.0	.0039	5,855	4,540	9.66	5.45	3.8	8.8	160.4	154.8	.791	29.7	.575
672	do	25	75	12 00	45	------	61.6	38.1	61.9	.0041	5,680	4,595	8.92	4.90	3.3	7.9	175.2	158.8	.798	27.0	.599
666	do	------	100	12 00	91	------	57.5	38.0	66.0	.0040	6,695	3,395	8.59	4.53	3.2	7.0	171.2	165.6	.791	27.0	.632
667	do	------	100	17 00	83	------	58.2	37.4	64.2	.0041	7,455	4,365	7.95	4.48	3.0	7.0	184.8	168.8	.785	29.2	.636
662	Caustic soda	75	25	12 00	42	------	60.9	42.5	69.8	.0040	7,540	6,270	9.63	5.33	3.2	8.5	142.4	158.4	.826	27.5	.700
663	do	75	25	14 00	38	------	60.6	41.9	69.1	.0039	7,275	9,735	9.97	5.54	3.2	8.7	148.4	144.4	.827	31.0	.866
669	do	75	25	10 00	45	------	60.5	41.6	68.8	.0040	6,495	6,410	9.49	5.29	3.2	8.9	155.6	140.4	.825	31.5	.640
683	do	75	25	[1]17 00	[1]34	23	54.8	38.9	71.0	.0037	5,000	2,605	8.48	4.67	3.6	8.0	139.2	128.0	.833	29.0	.793
684	do	75	25			26	57.8	42.2	73.1	.0039	4,840	2,945	8.84	5.03	3.3	8.0	141.6	141.6	.860	27.5	.751
685	do	75	25	13 00	23	15	58.4	46.7	79.9	.0039	4,425	4,680	9.74	5.35	3.6	7.9	146.8	140.4	.843	27.0	.723
686	do	75	25	13 00	23	15	60.3	43.6	72.3	.0039	5,300	4,770	9.24	5.36	3.2	8.4	140.8	133.2	.826	27.0	.688
694	do	75	25	13 00	27	26	61.5	43.7	71.1	.0040	8,000	5,900	9.73	5.30	3.5	9.3	155.2	159.2	.846	30.5	.837
695	do	75	25	16 00	29	24	59.4	45.6	76.8	.0039	8,040	5,310	9.80	5.33	3.4	9.6	152.8	149.6	.839	32.0	.701
696	do	75	25	11 00	33	30	58.2	45.0	77.4	.0038	8,010	6,900	10.03	5.23	3.2	8.4	157.6	149.6	.856	23.0	.567
697	do	75	25	16 00	30	26	61.7	42.1	68.2	.0040	7,410	5,700	9.66	5.33	3.0	8.1	156.8	153.6	.851	23.5	.513
699	do	50	50	13 00	37	33	61.0	43.5	71.4	.0038	6,560	6,380	9.58	5.09	3.5	9.4	162.0	152.0	.803	29.5	.400
700	do	50	50	17 00	35	33	59.2	41.9	70.8	.0038	7,810	5,710	9.14	5.12	3.0	9.0	163.6	163.6	.826	29.0	.375

[1] 300-pound beater used. See explanation, p. 912.

TABLE 1.—*Data on unsized papers*—Continued

A. TESTS WHOLLY AT BUREAU OF STANDARDS—Continued

Machine run No.	Chemical used in cooking	Fiber composition		Beating interval	Freeness of stock		Physical tests												Chemical test, copper No.
		Linen	Cotton		After beating	At head box	Weight, 25 by 40 inches, 500 sheets	Bursting strength	Ratio of bursting strength to weight, 25 by 40, 500 sheets	Thickness	Folding endurance		Tensile strength (strip 15 by 100 mm)		Elongation		Tearing strength		Opacity	Gloss	
											Machine direction	Across machine direction	Machine direction	Across machine direction	Machine direction	Across machine direction	Machine direction	Across machine direction			
		Per cent	*Per cent*	*Hr. Min.*			*Pounds*	*Points*	*Per cent*	*Inch*	*Double folds*	*Double folds*	*kg*	*kg*	*Per cent*	*Per cent*	*g*	*g*		*Per cent*	
703	Caustic soda	50	50	[2] 12 00	[2] 35	32	60.5	43.1	71.2	0.0039	7,670	6,550	9.74	5.19	3.5	9.6	163.2	159.2	0.840	30.0	0.476
704	do	50	50	([3])	[2] 34	30	61.3	44.2	72.1	.0040	9,470	6,690	9.98	5.40	3.5	9.9	163.2	149.2	.832	31.0	.498
701	do		100	18 00	72	54	59.1	34.1	57.7	.0038	8,740	3,710	7.87	4.19	2.5	7.3	176.0	169.6	.817	28.0	.262
702	do		100	13 00	85	66	59.4	34.8	58.6	.0039	7,660	3,180	8.01	4.35	2.5	7.3	196.0	175.2	.818	32.0	.280
B. TESTS IN COOPERATION WITH COMMERCIAL MILLS																					
674				14 00	50	46	60.6	40.1	66.1	0.0042	3,910	3,100	8.62	4.90	3.3	7.5	177.2	167.2	0.921	27.4	0.576
Mill A							57.2	39.8	69.5	.0050	4,650	2,540									
681					33	25	59.4	35.8	60.3	.0037	3,890	1,050	8.41	4.22	3.6	9.3	128.8	119.6	.840	27.0	.640
682				12 00	29	27	60.0	39.1	65.1	.0040	5,710	2,960	8.86	4.90	3.2	9.5	155.6	154.8	.854	29.0	.598
Mill B–1							56.8	39.0	68.6	.0046	4,412	1,920									
692					38	40	58.9	38.2	64.8	.0039	4,935	2,680	8.46	4.57	3.1	8.4	148.4	137.6	.870	28.9	.632
693				14 00	43	29	59.6	41.9	70.4	.0038	6,390	5,415	9.51	5.31	3.2	8.6	169.2	150.0	.852	30.5	.613
Mill B–2							56.6	39.9	70.5	.0049	3,870	2,750									
730		75	25	14 00	27	25	59.0	42.0	71.1	.0038	6,540	6,400	9.70	4.80	3.4	9.7	144.8	138.4	.822	30.5	.562
731		75	25	12 45	39	38	60.0	40.0	66.6	.0038	5,670	3,395	9.10	4.80	3.5	8.8	146.4	142.8	.833	30.5	.644
733		75	25	14 00	31	32	60.0	39.0	65.0	.0040	5,760	3,630	9.00	4.80	3.1	8.5	160.8	151.2	.857	29.0	.690
Mill C							57.6	42.9	74.5	.0045	5,600	5,415									

[2] Cotton and linen beaten separately, 12 hours each. Freeness readings for beaten stock, 104 and 24, respectively; for mixture, 35.
[3] Cotton and linen beaten separately, 12 and 14 hours, respectively. Freeness readings for beaten stock, 92 and 25; for mixture, 34.

The strength tests show, in general, the resistance of the paper to a rupturing force. Variation in the method of application of the force permits measurements of the different qualities reported in the table as bursting, folding, tensile, elongation, and tearing strengths. The suitability of paper for currency use depends not only upon its strength and durability but also upon its ability to meet the printing requirements. Although the waterleaf or unsized paper is tub-sized before being submitted to the printing operation, the uniformity and general surface condition of the waterleaf sheet are factors in the results obtained. There are no tests to measure these qualities numerically, but they should be considered with the other physical properties in the final evaluation of the paper.

Figure 3 shows graphically the relative characteristics of four papers, of different fiber proportions, as compared with their mean values. Since the relative importance of the several characteristics is still a matter of personal judgment, the results for each are reduced to the same relative basis. The average value (25 per cent) of the four samples is taken as the reference basis (zero) in each case.

1. STOCK PREPARED FROM LIME-COOKED RAGS

(*a*) 75:25 LINEN-COTTON MIXTURE.—*Run No. 658.*—The manipulation of the beater roll for this run followed that described in Technologic Paper No. 329, page 98. At the end of 12 hours of beating, however, the stuff still contained small lumps of bunched fibers, commonly called "nits," and the fibers were too long. The beating was therefore continued until these conditions were corrected, 16½ hours being required for the complete operation.

After the stuff was dropped to the chest, examination of the beater roll showed that the fly bars of the roll were touching the bedplate bars only at one end. Owing to this condition the actual beating surface was much decreased in area and, therefore, more time was required for the beating than in the preceding case to which reference was made. The beater roll was subsequently leveled and adjusted, as was also the lighter bar, before the next test was made.

The measurements of the paper show it to be as strong as that made in the earlier work.

Run No. 659.—The beater roll was lowered more slowly for this run than for run No. 658. At the time the beating was in progress the stuff prepared for run No. 658 had not yet been run over the paper machine, but judging by the sound of the beater roll it seemed advisable to beat the furnish more gradually. The fibers were well frayed and the stuff freed from nits at the completion of the process. As shown in Table 1 the paper differed little in folding endurance from that of run No. 658.

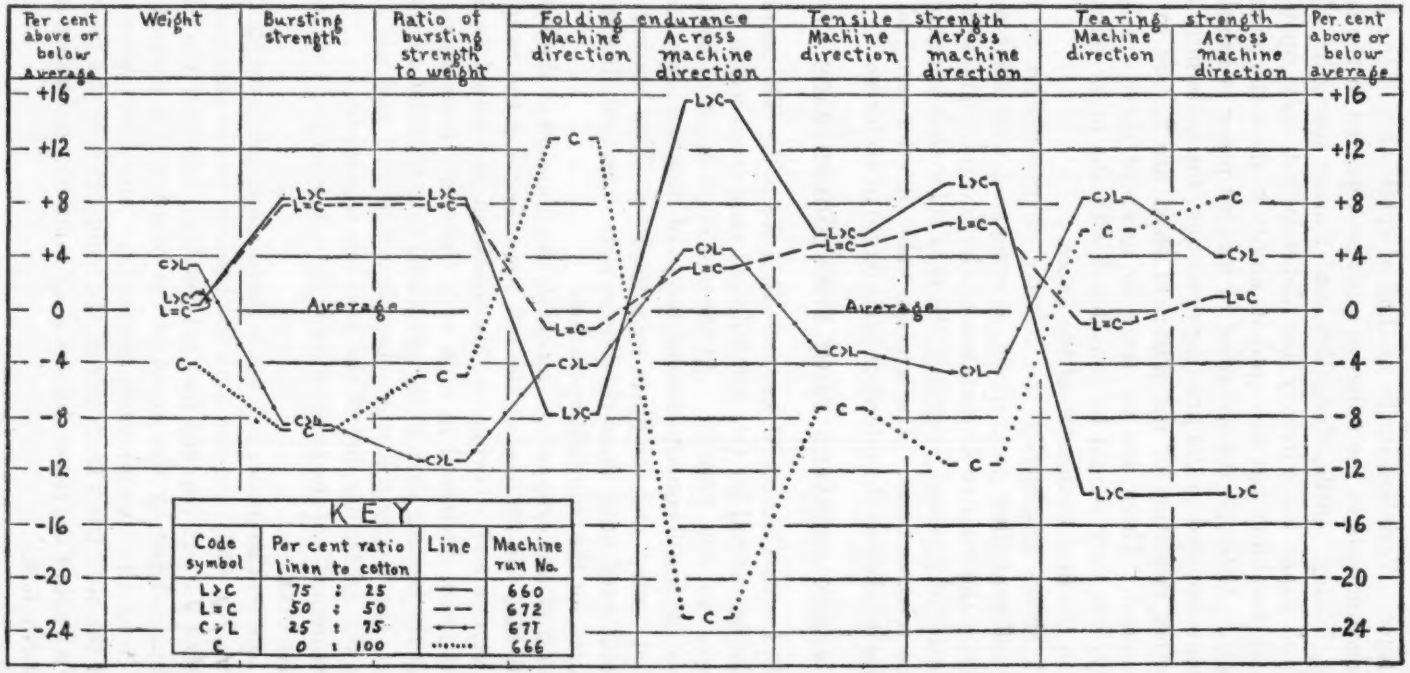

FIGURE 3.—*Relative characteristics of four experimental papers produced in the research to enhance the quality of national currency paper*

Read each column independently and only for the relative values compared with the average for that characteristic. Owing to the different utility of the several characteristics, no intercomparison is here made between the magnitudes in the different columns.

Run No. 660.—Satisfactory paper having been produced in the two preceding runs, the stuff for run No. 660 was prepared in accordance with the procedure previously determined as best for a 75:25 mixture (Technologic Paper No. 329) and accepted as standard for the bureau work. Since the test procedure duplicated that for run No. 542 of the earlier work (Technologic Paper No. 329, p. 104), it was expected that the measurements on the paper would agree with those obtained for the earlier run; and inasmuch as the condition of the stock for the runs appeared to be the same, would agree with the measurements for runs Nos. 658 and 659 also. The data obtained confirmed the belief that under controlled and duplicated test conditions practically duplicate results are produced.

Run No. 661.—This run differs from run No. 660 only in that the beating was continued two hours longer at the brushing point, zero setting of the roll. Beating for two hours at setting $-\frac{1}{2}$ followed, as in the preceding runs. The measurements show the paper to be of good strength, but no better than that made from stock beaten the standard way (run No. 660).

Run No. 668.—This run was not made primarily to obtain additional data for the investigation, but to demonstrate to a group of visiting manufacturers of fine rag papers the methods employed at the bureau in the research on the production of currency paper. The standard beating procedure was followed in preparing the stock. The paper made was apparently as strong as the other papers, but the appearance of the sheet was not as good as usual. When discharged from the beater the stuff contained some long fibers and the Jordan was not large enough to handle it properly. As a result, the stock going to the machine was more or less lumpy, and consequently crushed spots appeared in the paper when calendered.

Run No. 670.—The silk fiber in United States currency has until recently been limited in distribution to two narrow bands in the paper, one on each side of the portrait on the printed currency. The Treasury Department was considering changing the specifications for the paper to require that the silk fibers be distributed uniformly throughout the sheet. Information as to the amount of silk fiber that would be needed was desired. Run No. 670 was made for that purpose and silk fibers were therefore incorporated in the stock as a distinctive feature.

The beating was according to the standard procedure, but at the end of 12 hours the stuff was not clear, not free from nits, and an additional hour was required to complete the operation. The presence of the silk caused no trouble in the paper-machine operation.

(*b*) 50:50 Linen-Cotton Mixture.—*Run No. 671.*—The beating was in accordance with the standard procedure, but an extra hour was required to clear the stuff.

(*c*) 25:75 LINEN-COTTON MIXTURE.—*Run No. 672.*—The half stuff was beaten according to the regular procedure.

(*d*) 100 PER CENT COTTON.—*Run No. 666.*—No difficulty was encountered in this run. The paper was well formed and appeared free from fuzz. The measurement also showed it to be very good in strength.

Run No. 667.—The beater roll was lowered much more slowly in the preparation of the stuff for this run than for the preceding. It was hoped that by increasing the beating time, decreasing the pressure of the beater roll proportionally, "slower" stock and consequently stronger paper would be obtained. The beating interval was 17 hours, but the paper did not show any appreciable increase in strength over that of run No. 666.

2. STOCK PREPARED FROM RAGS COOKED WITH CAUSTIC SODA

Except that caustic soda was used instead of lime in the cooking liquor for the rags, the paper-making procedure for the remainder of the runs also was the same as that described in the earlier publication. The amount of caustic soda added differed with the character of the rags furnished to the boiler. The amounts used for the different kinds of cooks are given on page 903.

(*a*) 75:25 LINEN-COTTON MIXTURE.—*Run No. 662.*—The stuff for this run was prepared in accordance with the regular method of beating. The paper made seemed to be softer than that made from rags cooked with lime. Table 1 shows it to have a higher folding endurance also.

Run No. 663.—The beating for this run differed from that for the preceding only in that the process was continued two hours longer when the roll was at the $-\frac{1}{2}$ setting. The measurements show that the paper produced had a higher folding endurance than that of run No. 662 (12 hours of beating).

Run No. 669.—The conditions relative to this run were the same as for the preceding two runs, except that the beating time was only 10 hours.

Runs Nos. 683 and 684.—The 50-pound beater was used in preparing the stuff for all the machine runs except Nos. 683 and 684. For these runs the 300-pound beater was employed. The beating procedure planned was an adaptation of the standard method suitable for the larger beater, but during the preparation of the stuff it was necessary to keep the beater roll at the +2 setting for 4 hours, because of an overload of more than 15 per cent on the motor. If there had been sufficient motor capacity, the roll would have been at the zero setting in 7½ hours, instead of being only at the +2 setting. Because of the insufficient motor capacity, the required beating time was increased to 17 hours. This fact should be considered in comparing

the test data for the runs. It is believed, however, that with a motor large enough to operate the beater, the results obtained with the 300-pound beater would compare favorably with those for the 50-pound one.

The beaten stuff was pumped from the Jordan directly to the paper machine. Screen plates with 0.024-inch slots were used for machine run No. 683, but 0.036-inch cuts were used for run No. 684. (The plates with the 0.024-inch openings were used for all the other tests.) The test data on the papers of the two runs are practically the same. Screening the stock through slots of different gage caused no resultant differences in the sheets.

In all the previous work the cotton rags, light-colored linen rags, and dark-colored linen rags had been kept separate throughout the conversion into half stuff. The beater charges were mixtures of the different half stuffs. For the remainder of the runs on stock composed of 75 per cent linen and 25 per cent cotton, however, the rags were all cooked together.

Runs Nos. 685 and 686.—Different methods were used in bleaching the half stuff for runs Nos. 685 and 686 to determine their comparative effect on the strength of the fiber. The boiler furnish was 75 per cent linen and 25 per cent cotton, and the chemical agent was 4 per cent of caustic soda. The cooked rags were divided into two equal lots. One part was washed, bleached, washed again, and beaten, without removal from the beater tub. Machine run No. 685 was on the stock thus prepared. The remainder of the cook was washed and after being partially bleached in the washer was discharged into the drainer, where the bleach was allowed to become spent and the final washing given the half stuff. The half stuff was beaten similarly to that for run No. 685. The stock was run over the paper machine as run No. 686.

The test data show very little difference in the papers. It apparently makes no difference in the quality of the paper whether the cooked rags are washed immediately after bleaching and converted into stuff without removal from the beater or whether the drainer system of bleaching is used and the washed half stuff then returned to the beater for the final reduction, providing, of course, that in the latter operation an excessive amount of bleach is not used. To prepare stuff commercially according to the first method, run No. 685, more beaters would be needed, however, and it is doubtful if the results obtained would warrant the increase in equipment required.

Runs Nos. 694 and 695.—In making the cook for these runs the rags were furnished to the boiler and allowed to stand therein overnight. The next morning the regular amount of cooking liquor was added. At that time it was noted that the boiler contained a greater volume of liquor than it had for any of the previous cooks. The

presence of the extra amount may have been due to the fact that the main water valve had been left open and the possibility that one of the valves at the cooker may have leaked. The greater quantity of water weakened the strength of the cooking liquor and also reduced the space in the cooker available for steam. Owing to the latter condition the usual cooking temperature could not be maintained, although greater pressure in the boiler was recorded. The pulp was reduced to half stuff and bleached in the usual way.

The beating procedure for run No. 694 was in accordance with the standard method. The time required was 13 hours. The stuff seemed much more harsh than usual, however, which condition was doubtless caused by the circumstances described relative to the cooking. Practically no trouble was experienced in running the stock over the paper machine, but the paper produced was harder than that made from the other caustic soda cooks.

The stock for run No. 695 was prepared by somewhat different beating procedure. After the beater was furnished the roll was set at +6 and was lowered at the rate of one-half turn an hour until the +½ position was reached. The total beating time was 16 hours. No difference was noted in the strength of the papers made in the two runs, however.

Runs Nos. 696 and 697.—In order to check the two preceding runs a similar cook was made. The half stuff was prepared in the usual way.

For run No. 696 the beating operation was in accordance with the standard procedure, and the time required was 11 hours. The test data for the paper check very closely with those for run No. 694, but the paper had a softer feel. Figure 4 is a photomicrograph[4] of the stuff as it was dropped from the beater, ready for the paper machine. The photomicrograph (also those of figs. 5 to 8) was made at a magnification of 100 diameters, but for the reproduction herein the magnification is about 60.

The beating procedure employed in the preparation of the stuff for run No. 697 was like that for run No. 695. The data for the paper of this run agree well with those for runs Nos. 694, 695, and 696.

(*b*) 50:50 LINEN-COTTON MIXTURE.—*Runs Nos. 699 and 700.*—A cook was made on a furnish of 50 per cent linen and 50 per cent cotton rags, with 3 per cent of caustic soda. Two paper machine runs, Nos. 699 and 700, were made on stock prepared from the cooked mixture. The beating intervals were 13 and 17 hours, respectively. The papers made seemed very good and compared very favorably in strength with papers made from 75 per cent linen and 25 per cent cotton stock.

Figure 5 shows the condition of the stuff for run No. 699 at the completion of the beating, 13 hours.

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[4] Photomicrographs were made by R. E. Lofton, associate physicist, Bureau of Standards.

FIGURE 4.—*A 75:25 linen-cotton mixture*

After completion of the beating (11 hours). Stock for paper machine run No. 696.

FIGURE 5.—*A 50:50 linen-cotton mixture*

After completion of the beating (13 hours). Stock for paper machine run No. 699.

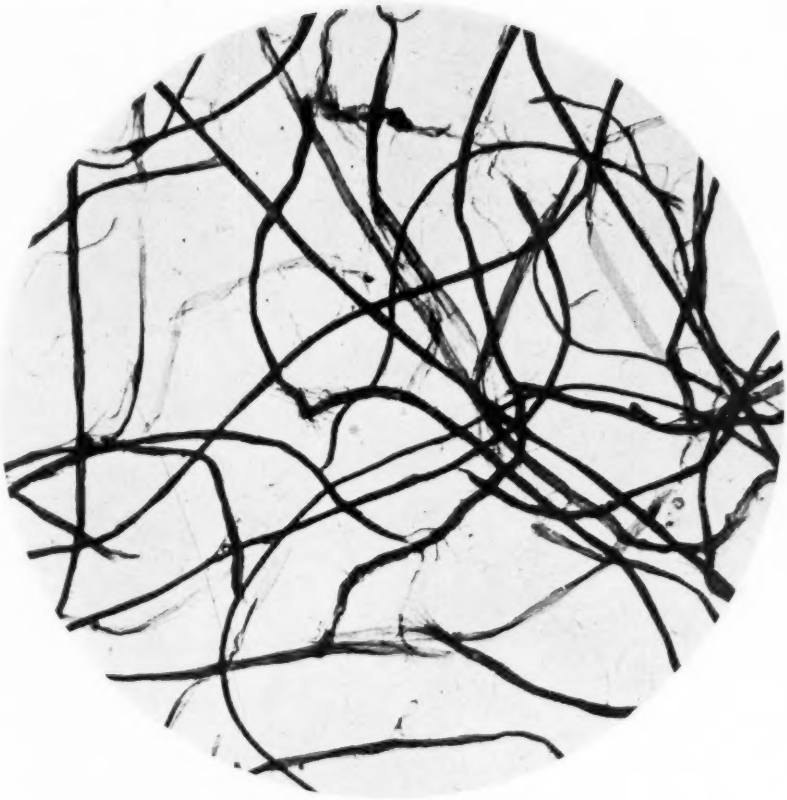

FIGURE 6.—*A 100 per cent cotton stock*

After completion of the beating (12 hours). Stock was mixed with linen before being run over the paper machine run No. 703.

FIGURE 7.—*A 100 per cent linen stock*

After completion of the beating (12 hours). Stock was mixed with cotton before being run over the paper machine, run No. 703.

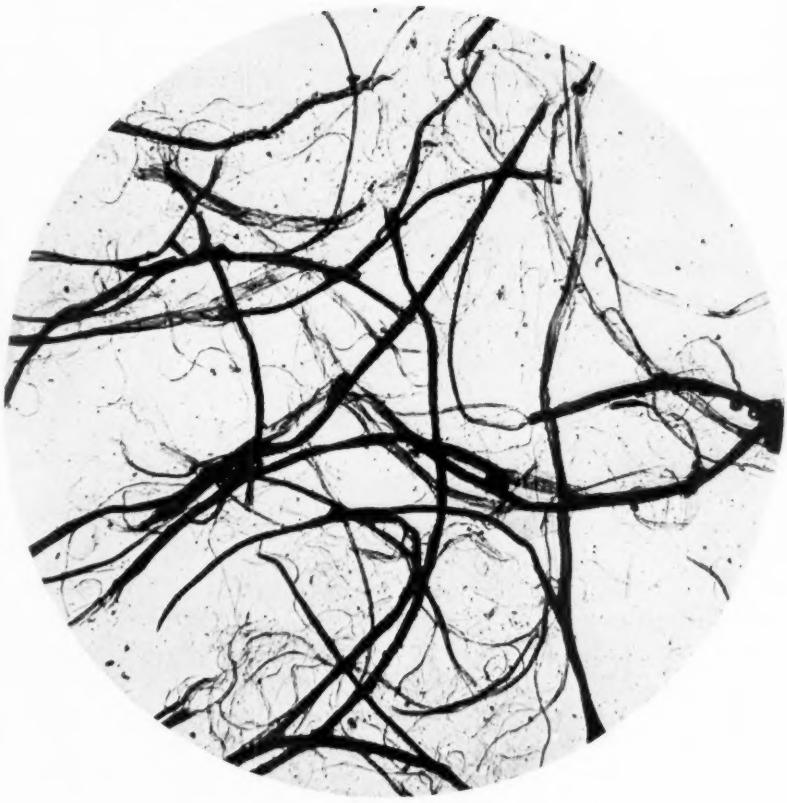

FIGURE 8.—*A 50:50 linen-cotton mixture*

The cotton and linen were beaten separately (figs. 6 and 7), and the stuffs mixed in the machine chest. Stock for paper machine run No. 703.

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Runs Nos. 703 and 704.—Preparatory to making runs Nos. 703 and 704 two cooks were made. The boiler furnishes were 100 per cent cotton and 100 per cent linen. The resultant pulps were kept separate throughout the preparation of the stuff. The beaten stuffs, the cotton and the linen, were mixed together in the machine chest.

The standard beating procedure was followed for machine run No. 703. The freeness reading for the cotton stuff at the completion of the beating was 104, and for the linen, 24. The reading for the final mixture was 35. Figure 6 shows the condition of the 100 per cent cotton stuff after the 12 hours of beating, and Figure 7, the condition of the 100 per cent linen stuff. The photomicrograph shown in Figure 8 is of the mixed stuffs, 50 per cent cotton and 50 per cent linen, and is therefore comparable with that of Figure 5.

For machine run No. 704 the cotton was beaten as for run No. 703, but the linen was given a longer brushing period. The beating intervals were 12 and 14 hours, respectively. The freeness reading for the cotton stock was 92; for the linen, 25; and for the final mixture, 34.

As shown in the table, the papers of runs Nos. 703 and 704 differ little in strength characteristics, but are somewhat superior to the paper of run No. 699, for which the cotton and linen half stuffs were mixed together in the beater, and for which the regular beating procedure was followed.

The freeness reading of the stuffs for runs Nos. 703 and 704 indicate that linen fibers have proportionally greater influence than cotton on the freeness of a mixture of these materials.

(*c*) 100 Per Cent Cotton.—*Runs Nos. 701 and 702.*—After the beater was furnished for paper machine run No. 701 the roll was set at +6 and was lowered at the rate of one-half turn an hour until the setting +½ was reached. The rate was then varied according to the condition of the stock. The total beating time was 18 hours. The standard beating procedure was employed for the stuff of run No. 702, and the beating interval required was 13 hours. Both runs were considered very good for 100 per cent cotton stock.

VII. PAPER-MAKING TESTS IN COOPERATION WITH COMMERCIAL MILLS

As before mentioned, fine paper of such great strength as that developed at the bureau in the currency investigation had not previously been produced commercially. As a result of the research, however, three manufacturers of fine rag papers instituted similar experimental tests on a commercial scale, and requested the assistance of the bureau in the development work. The cooperative study included visits to the commercial mills in an advisory capacity, and paper-making tests at the bureau and in the commercial mills for comparison of their respective manufacturing processes. Table 1

includes data on the papers produced. The commercial mills are designated therein as "A," "B," and "C."

1. MILL A

Run No. 674 was made in the bureau paper mill from half stuff received from manufacturer A. Paper made in mill A from half stuff from the same batch was also submitted and is listed in the table as mill A.

During the beating of the half stuff in the bureau mill the beater roll was lowered very gradually, and not below the brushing point. The appearance of the finished sheet was very good but the feel was harsh, not soft and smooth as that of the bureau papers had been. The half stuff furnished to the beater was likewise harsh, as if it contained much more cotton than linen fiber.

Although the folding endurance measurements show the paper made at the bureau to be more uniform in formation, the semicommercial work checks the commercial run very satisfactorily, as indicated by the test data. Compared with papers of the previous bureau tests, however, the test results indicate that the rags used in mill A were not of as good paper-making quality as those employed at the bureau.

2. MILL B

Stock, half stuff, and paper samples, representing the same fiber at the corresponding stages in the manufacturing process, were submitted by mill B. Papers made at the bureau from the stock and the half stuff are indicated in the data by runs Nos. 681 and 682, respectively. Measurements on the paper samples submitted appear under the designation mill B–1.

The prepared stock submitted was described by the manufacturer as "wet stock taken from the doctor on the couch roll, which represents our beaten, jordanned, and screened fiber ready to be made into paper."[5] Preparatory to running it over the bureau's paper machine, the stock was mixed with water in the beater to the consistency regularly used in the bureau tests. It was then dropped to the beater chest and from the chest was run through the screen to the paper machine. The test data for run No. 681 are on the paper made from this stock.

The formation and appearance of the sheet were very good, but the strength was less than that of the paper sample submitted for the same stock. This condition was expected, however, as it has been the experience of the bureau that stock screened and run over the paper machine a second time does not give as strong a sheet as that

[5] A doctor is a scraper employed to keep the surface of a roll clean. By its use here the wet stock was removed from the machine.

made in the original run. Much better comparison of the corresponding processes in the two mills would have been afforded if the stock sent by manufacturer B had been taken before being screened but after it had passed through the Jordan refiner. The stock used at the bureau would then have been comparable in condition to that going onto the paper machine in the commercial mill.

The half stuff received from manufacturer B was shorter than that regularly prepared at the bureau in the experimental work. It appeared to have received too much cutting, but not enough brushing. The subsequent beating, jordanning, screening, and paper-machine operation were in accordance with the procedure at the bureau. The appearance and formation of the paper produced were fairly good, but the folding endurance was not as nearly uniform in the two directions of the sheet as for the papers made wholly at the bureau. The greater difference was probably due to the fibers having been cut more and brushed out less in the preparation of the half stuff at mill B.

The bureau suggested that if manufacturer B desired additional comparative tests, the stock submitted be taken after the jordanning but before the screening, and the half stuff supplied be prepared by more brushing and less cutting in order to have the fibers long but well frayed. Manufacturer B wished to have further data and submitted additional test materials accordingly. Machine runs Nos. 692 and 693 and the data designated mill B–2 are for the latter materials.

The stock received was, as before, mixed in the beater to the consistency used for the bureau work, discharged into the beater chest, and thence run through the screen to the paper machine. The paper made from this stock should be more nearly comparable to that made in the experimental run in the commercial mill. As noted in the table, runs Nos. 692 and mill B–2 check very closely. The data show that with the same stock the results obtained on the bureau's semicommercial paper machine check those obtained in a commercial mill.

The half stuff received was given 14 hours of beating. On completion of the process the fibers were of good length and the stuff was clear and appeared in condition to give a good sheet. The stock was pumped from the Jordan directly to the paper machine for run No. 693.

Comparison of the test data shows that paper made from manufacturer B's half stuff, beaten in the bureau mill in accordance with its regular procedure, has approximately twice the folding strength of that made from the stock prepared in mill B from the same half stuff. It will be noted also that the folding endurance is much more nearly uniform in the two directions of the sheet, and it is believed that with papers of this type there is less distortion in the printing

operation. Any dissimilarity in the two lots of stock must have been due to difference in methods of beating. The beating procedure recommended by the bureau in its earlier publication on the production of experimental currency paper—that is, very gradual application of roll pressure—proved more satisfactory than manufacturer B's method.

3. MILL C

As a part of the commercial development of the type of paper produced experimentally in the currency research, manufacturer C submitted three boxes of half stuff for tests to determine the effect of temperature on the stock in the beating process. Paper made in the mill from the same batch of half stuff was also received. Three beaters of stuff were prepared at the bureau, each at different temperature. The corresponding paper machine runs made were Nos. 730, 731, and 733.

For the first machine run, No. 730, the half stuff was beaten according to the bureau's regular procedure. The beating time was 14 hours. The paper of the run was well formed and checked closely the strength of the paper sample submitted by mill C.

For machine run No. 731, the beating was practically according to the bureau practice, but after 7½ hours of beating the temperature of the furnish was raised approximately 30°— to between 148° and 153° F.— the beating being uninterrupted meanwhile. Since the increased heat expanded the bars in the roll and the bedplate, the subsequent beating action was harder than that for the previous run, No. 730, and the reduction of the stock was therefore more rapid. The stuff was dropped to the machine chest after 12¾ hours of beating and was then shorter than that for run No. 730.

In rinsing the stuff from the beater, cool tap water was used. The temperature of the diluted stuff in the machine chest was 105° F. A hand sheet made from the stuff just before it was discharged into the chest was of a brownish cast in color, but a sheet made from the cooler stock in the machine chest did not show the brownish color.

The half stuff for run No. 733 was given easier beating treatment. The roll was lowered only one-half turn an hour and the final setting was +½. After the first day of beating, 6 hours and 40 minutes, the temperature in the beater was gradually raised during the remainder of the operation. The beating time required for the stuff was 14 hours and the final temperature was 149° F.

Instead of the beater contents being dropped to the chest on the completion of the beating, the stuff was allowed to stand in the beater and cool down gradually, to permit the maximum injury to the stock by the heat. The following morning after the stuff in the beater was circulated and its temperature found to be 120° F., steam was again turned on and the temperature raised to 150°. The stuff

was then rinsed from the beater into the chest with warm water. The final temperature in the chest was 123° F.

Although the lowest roll setting was only +½, the increased heat in the beater had expanded the bars in the roll and bedplate and caused the subsequent beating action to be much harder than that for run No. 730.

Judged by general appearance there was practically no difference in the color of the papers of the three runs. As was expected there were differences in the strength values of the sheets, because of the harder beating given when heat expanded the roll and bedplate bars. The effect of the heat produced by the beating action on the fibers may be different, however, from that occurring at similar temperatures obtained by the application of steam.

The temperature in the beater is, of course, lower when soft, well-cooked pulp is used than when harsher, undercooked material constitutes the furnish. The beating action is more rapid, and therefore the time required for the reduction is less for the softer furnish.

VIII. GLUE SURFACE-SIZING TESTS

Currency is printed from engraved metal plates. In order that the fine lines may print with clear definition the paper is dampened. The sunk engraving is filled with ink and the dampened paper is forced against the plate by great pressure to withdraw the ink and receive the impression. The excellence of the printing on the finished currency is the main hindrance to effective counterfeiting.

The wetting quality of the paper is an important factor in the printing results. Any considerable variation in the resistance to wetting interferes with the mechanical handling of the paper during the conversion into currency and influences both the quality and the quantity of the finished work. Printing tests on various samples of experimental currency papers have shown that printing of superior merit can be produced on unsized paper, but that such paper requires extraordinary care in wetting, printing, drying, and incidental handling through the course of operations. Surface sizing is considered a requisite for satisfactory printing results on a production basis with the wet intaglio process, but the further work contemplated may show that the sizing operation can be eliminated.

The properties imparted to paper by surface sizing afford a means of control of the degree of wetness of the paper. The wetting quality is affected considerably by the amount of sizing present. To give currency paper as good printing quality as possible, experimental tests were made to determine the amount of glue sizing necessary to avoid interference with production. It was hoped that lighter sizing would suffice and that the printings would therefore approach the desirable characteristics of the unsized sheets. The sizing tests were

made in the paper mill of the Bureau of Standards, and the subsequent printing tests were made at the Bureau of Engraving and Printing.

To establish a standard procedure for applying glue sizing to the paper-machine products, preliminary tests were made to determine the comparative value of alum and formaldehyde as glue preservatives, and the effect of the temperature of the glue bath. Two sizing solutions were employed. The glue content of each was 6 per cent, but one contained alum as the preservative and the other formaldehyde. The proportions of alum and formaldehyde added were representative of commercial practice and, based on the weight of the glue, were 6 per cent and ¼ per cent, respectively. One grade of waterleaf or unsized paper was used throughout the tests. Four runs were made with each solution. The treated papers were calendered and tests were made thereon. The data obtained are reported in Table 2. In addition to the physical properties reported for the corresponding unsized papers in Table 1, the resistance of the moist paper to abrasion is also included. Currency in service is often subjected to handling with moist hands and the wet-rub test[6] is believed to simulate these conditions.

[6] The apparatus and method of test were developed at the bureau and are described in a previous article, A Wet-Rub Tester for Paper, by F. T. Carson and F. V. Worthington, Paper Trade J., 84, No. 2, pp. 43–44; Jan. 13, 1927.

TABLE 2.—*Data on surface-sized papers*

Paper machine run No.	Surface-sizing run No.	Glue in sizing solution	Glue preservative		Temperature of sizing bath	Physical tests																Chemical test—Size
			Kind	Amount, based on glue in bath		Weight, 25 by 40 inches, 500 sheets	Bursting strength	Ratio of bursting strength to weight, 25 by 40, 500 sheets	Thickness	Folding endurance		Tensile strength (strip 15 by 100 mm)		Elongation		Tearing strength		Opacity	Gloss	Wet rub	
										Machine direction	Across machine direction	Machine direction	Across machine direction	Machine direction	Across machine direction	Machine direction	Across machine direction				
		Per cent		*Per cent*	*° F.*	*Lbs.*	*Points*	*Per cent*	*Inch*	*Double folds*	*Double folds*	*kg*	*kg*	*Per cent*	*Per cent*	*g*	*g*		*Per cent*	*Double rubs*	*Per cent*
	Waterleaf					59.0	39.9	67.6	0.0042	2,865	1,435	9.04	4.96	1.6	6.0	140.0	124.0	0.918	28.5	22	1.97
	117A	6.0	Alum	5.0	120	61.2	58.1	95.0	.0032	3,330	2,670	10.68	6.54	4.2	8.9	121.2	116.0	------	------	36	2.55
	117B	6.0	----do	5.0	130	61.0	55.8	91.5	.0041	3,275	3,020	10.64	6.26	4.2	9.1	119.6	113.2	------	------	38	2.53
	117C	6.0	----do	5.0	140	58.9	55.7	94.5	.0040	3,460	2,400	9.97	6.00	4.4	8.4	108.0	98.4	------	------	45	1.83
	118	6.0	----do	5.0	130	59.6	56.8	95.3	.0040	3,680	2,850	10.32	6.09	4.5	8.5	110.8	106.0	------	------	31	3.11
	119A	6.0	Formaldehyde	.25	120	61.4	65.0	106.0	.0042	3,640	3,740	11.96	7.19	4.6	9.2	103.6	100.4	------	------	32	3.17
	119B	6.0	----do	.25	130	62.4	63.0	101.0	.0042	3,640	3,355	11.66	7.27	4.3	9.1	104.8	100.4	------	------	32	2.97
	119C	6.0	----do	.25	140	60.9	63.0	103.5	.0041	3,405	3,250	10.99	6.90	4.3	9.3	105.6	103.2	------	------	32	3.37
	120	1.0	----do	.25	130	62.0	62.2	100.4	.0042	3,220	2,110	11.47	7.01	4.8	9.3	106.4	101.2	------	------	41	3.21
658	121	2.0	----do	1.0	130	63.0	63.4	100.7	.0035	10,615	9,000	11.41	6.74	5.7	13.6	116.4	112.4	------	37.5	30	1.24
659	122	2.0	----do	.25	130	60.7	65.7	108.2	.0038	6,785	8,300	10.95	6.56	5.4	10.6	128.0	134.0	------	28.0	27	1.37
660	123	1.0	----do	.25	130	61.9	55.5	89.6	.0038	7,380	6,390	10.08	6.48	4.4	10.6	129.2	134.0	------	30.0	18	1.07
661	124	4.0	----do	.25	130	62.6	71.9	114.9	.0039	8,020	7,430	12.56	7.21	5.3	11.7	116.4	121.6	.832	23.5	42	2.00
668	125	4.0	Alum	7.0	130	65.6	64.0	97.6	.0042	7,920	9,170	11.69	6.91	5.0	9.9	157.6	150.4	.848	25.5	32	1.53
671	126	4.0	Formaldehyde	.25	130	65.1	76.0	116.8	.0040	9,020	9,270	12.89	7.59	4.9	10.9	140.4	132.4	.842	24.0	39	2.16
672	127	4.0	----do	.25	130	62.5	70.6	112.9	.0040	8,480	9,080	12.07	7.28	5.0	10.5	152.0	131.2	.798	23.0	35	2.59
666	128	4.0	----do	.25	130	59.0	70.9	120.2	.0039	8,960	8,390	11.61	6.98	4.9	10.0	139.6	138.0	.787	23.0	30	2.99
662	129	4.0	----do	.25	130	63.8	71.0	111.3	.0041	8,520	7,830	12.68	7.56	5.3	11.9	130.0	123.6	.840	25.0	36	2.48

For the first three surface-sizing runs, the temperature of the glue bath was 120°, 130°, and 140° F., respectively. Each run was made on the day that the glue solution therefor was prepared. To determine whether the age of the glue solution was a factor in the results obtained, the solution for the fourth run was permitted to stand in the vat three days at room temperature. Upon examination at the end of that time no bacterial growth was observed on the surface of the solutions and no deterioration or change in odor was noted. The solution containing alum had jellied, however, but that to which the formaldehyde had been added had the liquidity of water. Both solutions were warmed to 130° F. for the surface-sizing runs.

The data of Table 2 indicate that the sized papers were somewhat stronger when formaldehyde was used as the glue preservative than when alum was employed. Other advantages in the use of formaldehyde are the absence of acidity in the sizing and the more uniform penetration of the glue solution because of its greater fluidity. The latter is of direct value, since such uniformity is essential to even distribution of moisture in the mechanical wetting of the paper preparatory to printing.

The constants accepted from the preliminary tests for use in surface sizing the experimental currency papers were 0.25 per cent of formaldehyde (based on the weight of glue) and 130° F. temperature. Since the tests did not show any advantage in aging the glue solutions, the solutions for the currency tests were used the day prepared. Nine additional surface-sizing runs were made. Measurements for the sized papers are included in Table 2 and data for the corresponding waterleaf sheets were given in Table 1.

The experimental currency papers employed for the first five surface-sizing runs were of 75 per cent linen and 25 per cent cotton fiber composition. The concentration of the glue solution was varied, and in one case the amount of formaldehyde. The runs were as follows.

Run No. 121.—The concentration of glue in the sizing bath for run No. 121 was 2 per cent and the proportion of preservative used was 1 per cent, based on the quantity of glue in the bath. The proportion of glue retained in the sized paper was 1.24 per cent. As shown in the table, the paper had a very high folding strength. The increased quantity of formaldehyde increased somewhat the hardening of the glue, which was doubtless the cause of the greater folding strength.

Runs Nos. 122 and 123.—The concentration of glue in the sizing bath for runs Nos. 122 and 123 was 2 and 1 per cent, respectively, and the corresponding proportions of glue retained in the sized papers, 1.37 and 1.07 per cent. One-fourth per cent of formaldehyde was used as the preservative in each solution.

Run No. 124.—The percentage of glue retained in the sized papers of the preceding three runs was, in general, only about one-half of that found in the commercial paper being used for the Government currency. To afford comparison of the experimental and commercial papers in the printing processes, particularly in the wetting operation, the concentration of the glue in the sizing bath for run No. 124 was increased to 4 per cent. The proportion of glue retained in the sized paper was 2.00 per cent.

Run No. 125.—Since the amount of glue in the sized paper of run No. 124 approximated that in the commercial papers, it was decided to make a similar run using alum as the preservative, as is general in commercial practice. The concentration of glue in the sizing bath was 4 per cent, as in the preceding run, and the proportion of alum, 7 per cent. The glue retention in the sized paper was 1.53 per cent, the decrease doubtless being due to the lesser liquidity of the sizing solution.

The surface-sized papers for runs Nos. 121 to 125 were submitted for printing tests by the regular processes at the Bureau of Engraving and Printing. Those of the first four runs wet without difficulty and caused no trouble in the printing. Even the paper with only 1.07 per cent of glue proved satisfactory, and excellent impressions were obtained upon it.

The paper of surface-sizing run No. 125, in which alum was used as the preservative, wet irregularly and required sorting, however, and some of the sheets needed to be rewet. These conditions further indicated that the glue sizing penetrated the sheet less uniformly when alum was used in the bath than when formaldehyde was employed.

The conditions subsequently adopted as standard for the remainder of the surface-sizing tests were 4 per cent glue solution as sizing bath, one-fourth of 1 per cent formaldehyde as glue preservative, and 130° F. as temperature of the bath.

Four additional surface-sizing runs were made. The papers for runs Nos. 126 to 128 were from lime-cooked stock, 50 per cent linen and 50 per cent cotton, 25 per cent linen and 75 per cent cotton, and 100 per cent cotton, respectively. Run No. 129 was on paper made from stock 75 per cent linen and 25 per cent cotton, pulped by the caustic-soda process.

It will be observed from Table 2 that the glue retention increased with increasing amounts of cotton; also, that the paper of run No. 129, 75 per cent linen and 25 per cent cotton, caustic-soda cooked, had a higher glue content than that of run No. 124, similar fiber composition but lime cooked. The greater glue retentions were due in a large measure to the greater softness of the waterleaf papers.

In comparing the test data of the surface-sized papers, Table 2, with those for the unsized sheets, Table 1, the effect of the surface

sizing is evident. It produced in all cases a marked increase in the bursting strength, tensile strength, and folding endurance of the papers. The folding endurance, which is used as the principal criterion of strength for currency paper, is several hundred double folds more for the sized than for the waterleaf sheet, although the unsized sheet itself had a very high resistance in this respect.

In the wet intaglio process used for printing currency, the paper is wetted, printed under high pressure on one side, and dried. These operations are then repeated when the other side of the paper is printed. Such treatment is inimical to glue sizing and there is a possibility that some of the strength imparted to the paper by the glue sizing is destroyed as a result of these operations. Tests of their effect on the strength of the paper have given conflicting results. In some cases there was apparently no loss in strength, while in other cases the paper had apparently lost all of its glue-sizing strength. Quite likely the effect of the printing processes varies with variations in them and in the properties of different lots of paper, but in no case have the printing operations been found to affect the basic fiber strength of the paper. From these considerations it is thought desirable to specify the strength of the unsized paper, as well as that of the sized. This practice is desirable also in the case of commercial rag papers where a high degree of endurance is desired.

It should be borne in mind in considering the sizing results described that they may not apply directly to commercial bonds and ledgers, as they are sized for a different purpose than is currency paper. The latter is surface sized primarily to make it work satisfactorily through the wetting operation of the printing process. In bonds and ledgers the primary function of the surface sizing is to give good writing and erasing quality to the sheet.

IX. SUMMARY AND CONCLUSIONS

A previous publication, Technologic Paper No. 329, described the earlier production of experimental currency paper in the Bureau of Standards semicommercial paper mill. The folding endurance of the paper, which is generally considered the test best adapted for indicating the probable resistance to continued handling, was double that of the commercial paper being supplied for Government use when the investigation was initiated. The increase in strength was attributed chiefly to the method of beating the fibers. The investigation also demonstrated the applicability of the experimental manufacturing procedure to commercial production. As a result of the study the folding strength specified in the current contract specifications for United States currency paper is more than triple that previously required, and paper meeting the requirements is being supplied without increased cost to the Government or in the manufacturing process.

The Treasury Department subsequently requested additional study of the paper manufacturing processes, with a view to further improving the quality of currency paper. Paper possessing the characteristics required of currency paper and having the strength of the experimental papers had not been produced commercially previous to the investigation. Following the earlier study several manufacturers of high-grade rag papers instituted experimental tests of similar nature and also requested the cooperation of the bureau in establishing the best manufacturing procedure. The present publication relates to the continued research at the bureau. The test results indicate the following conclusions:

Either caustic soda or lime can be used satisfactorily as the cooking chemical in the production of paper of currency quality. The test papers made from half stuff prepared by the caustic-soda process were fully as strong as those made from lime-cooked stock and had a softer feel, making them, therefore, somewhat better in printing quality.

Caustic soda cooking solution has its maximum strength at the time added to the rags, and since caustic soda is a strong alkali, it may, therefore, injure the paper-making fiber if used in excess. It is important that the initial solution be of definite concentration, and control methods should be used in its preparation to insure the proper strength. The sodium salts formed with the impurities in the rags during boiling are soluble in water and can be readily washed out after the boiling is finished. Rags cooked with caustic soda are therefore comparatively free from deleterious impurities.

Lime is a comparatively weak alkali and only a small amount is in solution and, therefore, in active form at a given time. (See Technologic Paper No. 329, p. 93.) There is therefore less danger of lowering the fiber strength by excessive chemical attack. Owing to the fact that lime salts precipitate on the fibers when cold, the compounds formed are practically insoluble and there is greater difficulty in thoroughly freeing the rags from the impurities in the washing process.

The results confirm the statement in the earlier publication that gradual application of roll pressure in the beating process was the chief contributing factor in the greater strength of the papers made at the bureau. It was again demonstrated that with the same raw materials a suitable change in beating practice doubled the folding strength of the finished paper.

The greatest strength was obtained with the 75 per cent linen and 25 per cent cotton composition, but the 50:50 combination of these fibers produced a strong sheet, of somewhat better printing quality. The folding endurance of the 50 per cent linen, 50 per cent cotton papers was, nevertheless, well above the contract specification for currency paper (3,500 double folds), and the use of that fiber com-

position is worth consideration by commercial manufacturers. It should be remembered, however, that fiber loss in cooking is greater for linen than for cotton and that paper made from these materials cooked together will therefore have a relatively larger percentage of cotton than the boiler furnish.

Because of differences in inherent physical characteristics, linen develops better cohesive properties in the beating process than cotton, and the surface of the paper made from it is therefore firmer and freer from fuzz. An all-linen composition, however, gives too hard a paper for currency use.

The folding strength is less uniform in the two directions of the sheet for cotton stock, and the tensile strength is lower for papers containing cotton. These conditions do not necessarily indicate lower fiber strength of cotton than linen, but may be due to the difference in the cohesive properties of the fibers. The higher tearing strength of the papers containing large proportions of cotton is also explained by the inherent physical nature of the fiber, twisted fiber having higher tear resistance than straight.

Surface sizing is considered essential for satisfactory printing results by the wet intaglio process. The excellence of the printing on the finished currency is the main hindrance to effective counterfeiting. Uniform wetting quality of the paper is necessary to facilitate production. Experimental sizing and printing tests indicated that 4 per cent concentration of glue in the sizing bath, one-fourth of 1 per cent formaldehyde as glue preservative, and 130° F. as temperature of the bath were the most satisfactory sizing conditions for currency paper.

Commercial mills following the procedure used at the bureau in the currency tests obtained papers of similar quality. Likewise, paper made at the bureau from beaten stuff prepared in a commercial mill gave results duplicating those obtained on the commercial machine. The comparative data show the applicability of the experimental tests to commercial production.

As a result of the investigation, the cooperating commercial mills are now producing a paper similar to that developed at the bureau. The improvement made is doubtless reflected in the quality of other rag-content papers also. It is believed that the test data will be of value in the general technic of paper-making.

WASHINGTON, April 3, 1929.

A METHOD OF MEASURING THE STRESS-STRAIN RELATIONS OF WET TEXTILES WITH APPLICATION TO WET RAYONS [1]

By Homer A. Hamm and R. E. Stevens

ABSTRACT

An immersion tank has been developed as auxiliary equipment for a recording stress-strain tester. This tank is built around the lower jaw of the testing machine. It is equipped with suitable stirrer, heater, and heat-control apparatus. The textile, in this method, is fastened in the jaws of the testing machine, liquid is poured in the tank, and after a suitable immersion period the break is made. The results of a series of tests on rayons broken dry, broken dry after wetting in water at 20° C. and at 100° C., and broken wet at various temperatures are given.

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I. INTRODUCTION

The stress-strain relations of wet textiles have become of increasing interest with the development of the rayon industry, as rayon is weakened considerably more by wetting than natural fibers. The handling of the usual textiles when wet offers no great difficulties. This is not the case with rayon, however, as producer and processor, laundryman, and consumer may testify. Therefore, a greater knowledge of the physical properties of wet rayons as obtained from a consideration of stress-strain relations is desirable.

[1] In this paper the term "rayon" denotes synthetic fibers of regenerated cellulose or of cellulose derivatives.

An auxiliary apparatus for the complete immersion of the sample during test has been designed for the ordinary testing machine and is adapted to testing wet textiles by the usual methods or by the improved multiple-strand[2] test. This apparatus and some results obtained on four types of rayon, wet with water at various temperatures, are described herein.

II. REVIEW OF PREVIOUS WORK

The methods used by earlier investigators for determining the strength and the elongation of wet textiles were somewhat similar, differing principally in the manner of wetting the samples and in the number of strands broken. P. Krais[3] gave a few results obtained by using single-strand tests on dry and wet rayons. J. Obermiller and M. Goertz[4] also broke single strands in their determination of the breaking strength of dry and of wet yarns. P. E. King and E. N. Johnson[5] made use of the single-strand test for measuring the tenacity and elongation of a wide range of samples of dry and wet rayon yarns. H. D. W. Smith[6] used the usual multiple strand method; a number of ends were thoroughly wet in water, fastened in the jaws of the testing machine, and broken. D. C. Scott[7] referred to a machine for testing textiles under water but included no details. R. A. Van Amburg[8] described a multiple strand test for wet textile yarns, the chief advantage of which is that the break is made as the partially immersed sample is removed from the liquid. He gave a few results on the breaking strength of wet and dry yarns, comparing his method with older ones.

These methods and results will be discussed only in a general way. Tests in which the yarn is partially immersed give the wet breaking strength only for textiles having a lower breaking strength when wet than when dry, and, therefore, this method of testing is not generally applicable. Furthermore, it is impossible to measure the elongation of the wet yarn under these conditions. The handling of wet rayons, as in those methods in which the fiber is wet before placing in the jaws of the testing machine, is to be avoided since rayon fibers are easily changed in physical properties when handled wet. Also evaporation of liquid from the sample before the break is made may affect the results of the test. The results of one investigator are not strictly comparable with those of another as conditions of test and samples tested are not identical.

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[2] C. W. Schoffstall and H. A. Hamm, B. S. Jour. Research, **2**, p. 871; 1929.
[3] P. Krais, Z. Angew, Chem., **39**, p. 196; 1926.
[4] J. Obermiller and M. Goertz, Melliand's Textilb., **7**, 163; 1926.
[5] P. E. King and E. N. Johnson, J. Soc. Dyers and Colourists, **44**, p. 346; 1928.
[6] H. D. W. Smith, Textile World, **70**, p. 2227; 1926.
[7] D. C. Scott, Textile World, **74**, p. 2623; 1928.
[8] R. A. Van Amburg, Textile World, **70**, p. 3627; 1926.

III. DESCRIPTION OF APPARATUS AND TEST PROCEDURE

1. FEATURES OF METHOD

The method here described was developed to embody the following features: (1) Immersion of the sample until conditions of equilibrium in the fiber have been obtained; (2) complete immersion during test; (3) use of the improved multiple-strand method of test to increase precision, dependability, and speed; (4) adaptability to different thermal conditions and liquids; (5) adaptability to other forms of textiles than yarns; and (6) the expression of results as stress-strain relations.

2. EARLIER APPARATUS AND TESTING PROCEDURE

The earlier apparatus for the immersion of samples consisted of a copper immersion tank fitted to the lower jaw of an ordinary testing machine. This lower jaw was fastened in place by allowing its bolt to pass up through the bottom of the tank. The lower jaw served as a nut and the part of its bolt that fastens on the testing machine as the head of the bolt. Rubber washers were used to prevent leaks. In determinations recorded below, this immersion tank was used, fitted on a Scott automatic recording 55 to 110 pound tester of the pendulum type. The time of immersion was selected arbitrarily as one-half hour, and the break was made with the sample immersed in the liquid.

In these tests sampling was done in accordance with the equitension lea method,[9] which has been shown to give a high degree of precision for dry yarns. Thus the test for the stress-strain relations of wet textiles was made to embody the essential features of tests in the dry condition and the results of wet and dry tests were, therefore, comparable. The equitension lea method has been replaced by the multiple-strand test,[10] which gives greater speed and adaptability. Tests run by the two methods were in accord.

After the samples had been inserted in the jaws of the testing machine, water at the proper temperature was added, care being taken by pouring the water down one side of the immersion tank, to prevent washing of the fibers. The temperature of the bath was regulated to within 1° C. by the application of hot plates. This method of temperature control, though accurate, was cumbersome and required much of the operator's time. Difficulty was also experienced in inserting the samples.

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[9] W. T. Schreiber and H. A. Hamm, Textile World, p. 97; Sept. 24, 1927.

[10] The equitension lea method was a step in the development of the multiple-strand test and as such is not a separate method. The study of wet rayons was made simultaneously with the development of the multiple-strand test.

3. LATER APPARATUS

A new Monel metal auxiliary apparatus, shown in detail in Figures 1, 2, and 3, was constructed so that all disadvantageous features of the older apparatus were eliminated. Figure 3 is a top view of the immersion tank showing the general arrangement of parts and the shape of the tank. This shape is necessary in order to use a minimum of liquid and to provide clearance for moving parts of the testing machine. The temperature of the bath is electrically regulated. Handholes are provided for inserting the sample.

4. TESTING PROCEDURE

The procedure for making a test is as follows:

1. Handhole plates, *A* and *B*, are removed. (Fig. 2.)
2. The dry sample is inserted, through handhole *A*, in the jaws of the testing machine, as is done in the multiple-strand test. In this test the yarn is wound, equally space, parallel and under uniform tension, upon a split U frame which is held together by a clamp. The first and last ends are fixed to the frame by gummed labels. The lower jaw of the machine is tightened through handhole *B*, and the clamp is then removed from the split U frame.
3. The handholes are covered.
4. Sufficient liquid at the correct temperature is slowly poured into the tank until the fibers are entirely immersed.
5. The stirrer is set in operation and the heaters are turned on.
6. A chart is inserted in the machine to record stress-strain relations.
7. Stirring and heating are discontinued just before a break is to be made.
8. The break is made in the usual way.
9. The water is drained through the petcock.
10. The machine is run to the starting position.
11. The clamps are taken from the jaws after removing the handhole plates.
12. The jaws are dried.
13. The chart is removed, and the apparatus is ready for another test.

The temperature regulator must be set for the proper temperature before starting a series of tests. The faces of the jaws are covered with rubber sheeting to prevent slippage of the fiber when testing.

5. PRECAUTIONS IN MAKING TEST

1. The jaws of the testing machine should be dry before inserting the fibers; otherwise some of the fibers may become wet, and consequently all fibers would not be inserted in the same way.
2. The stream of water, as the water is poured into the tank, should be directed away from the yarns.

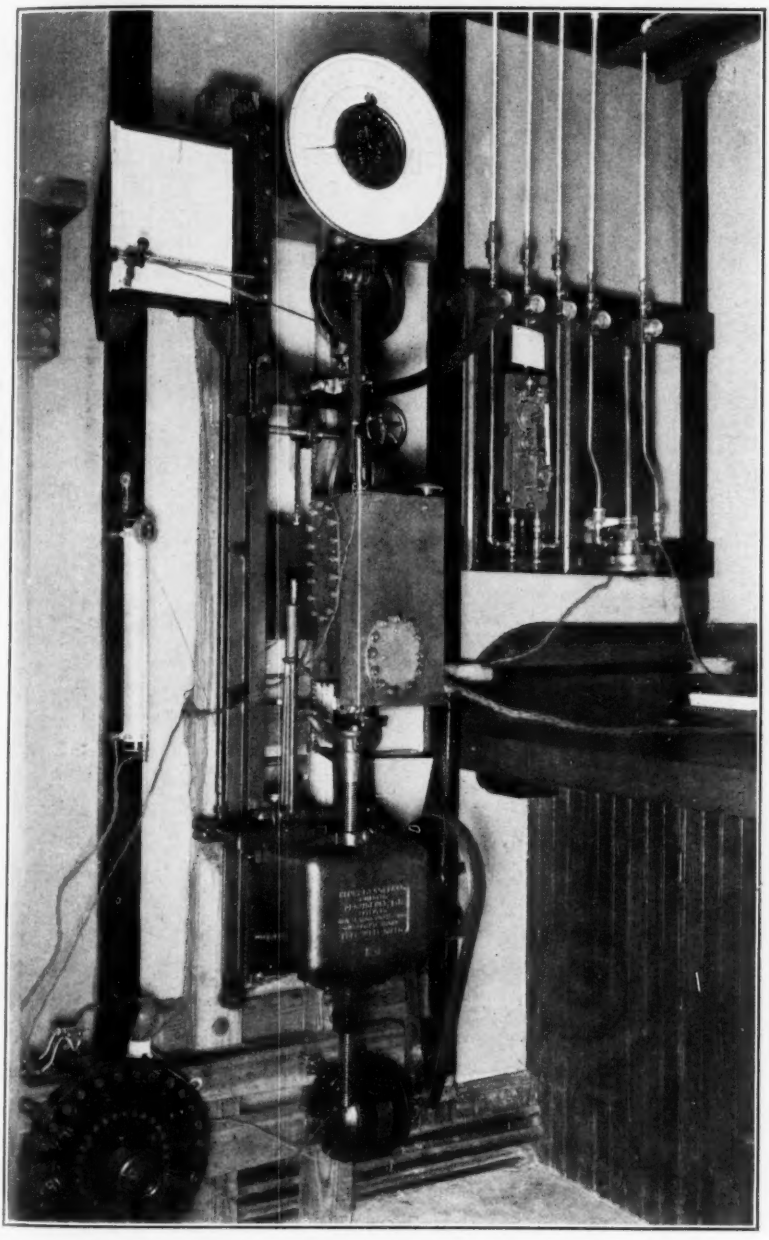

FIGURE 1.—*Auxiliary apparatus on the tester ready for operation*

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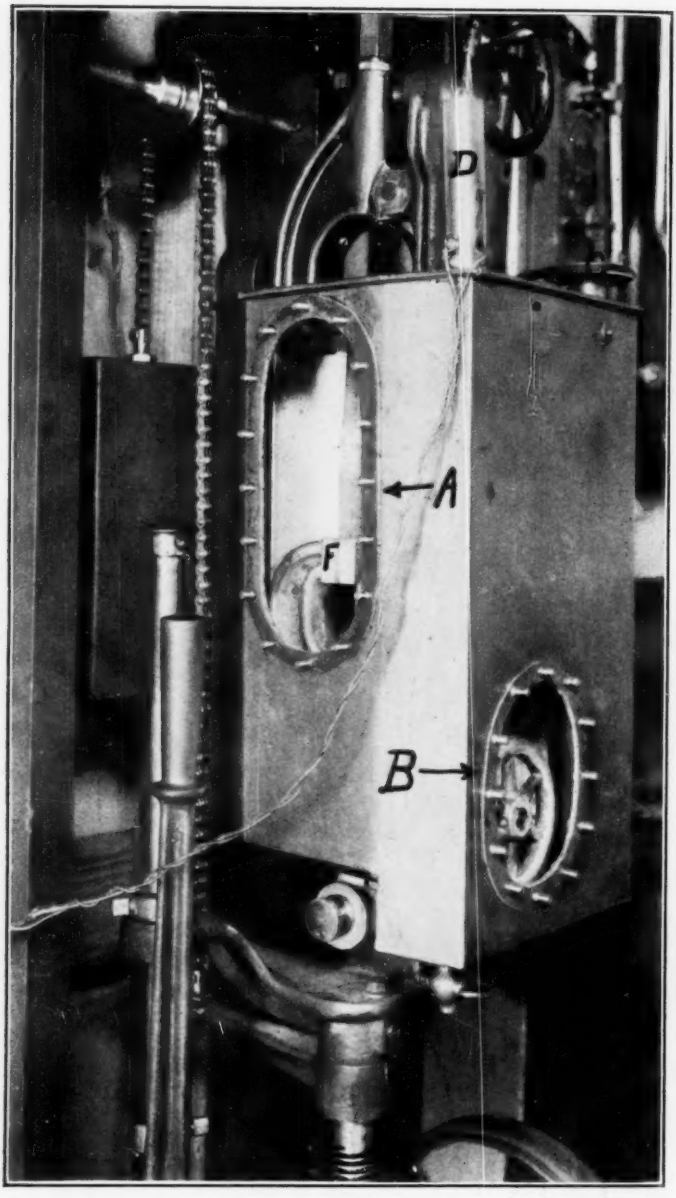

FIGURE 2.—*Left side view of immersion tank with manhole covers removed*

A, Manhole A; *B*, manhole B; *C*, stirrer; *D*, temperature control; *E*, upper jaw of testing machine; and *F*, lower jaw of testing machine.

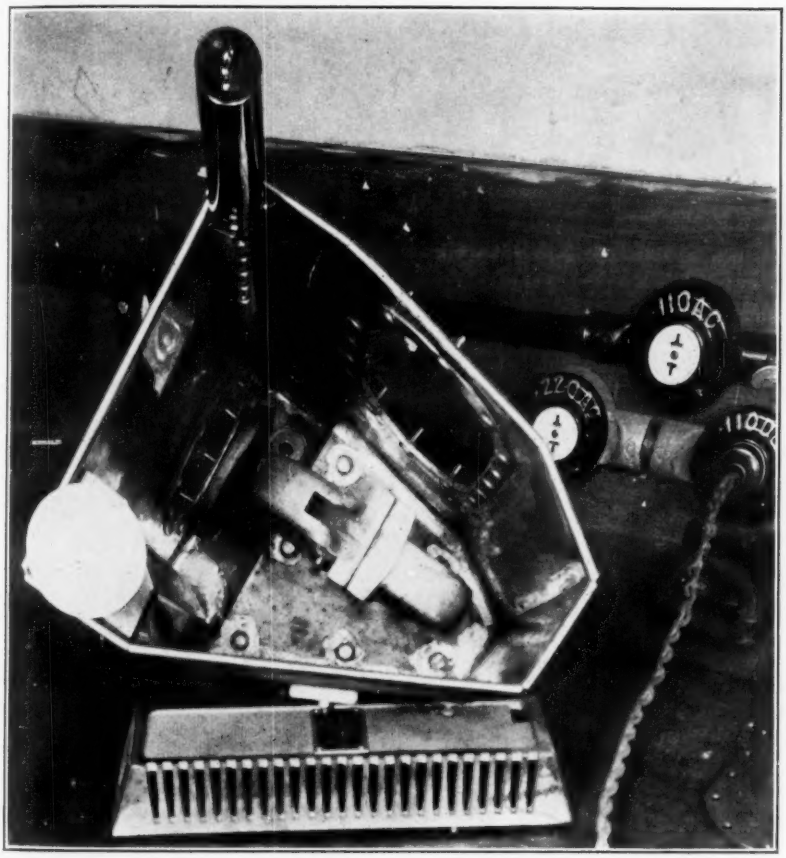

FIGURE 3.—*Top view of immersion tank showing inside details*

3. To prevent rusting, the moving parts which are immersed in water should be well oiled.

4. All samples before testing should be conditioned [11] so that comparable results on the elongation of the yarn upon wetting may be obtained.

6. INTERPRETATION OF STRESS-STRAIN CURVES

Considerable information concerning the physical properties of wet yarns can be obtained from the stress-strain curve of each test. Figure 4 is a typical stress-strain curve for wet rayon. The break-

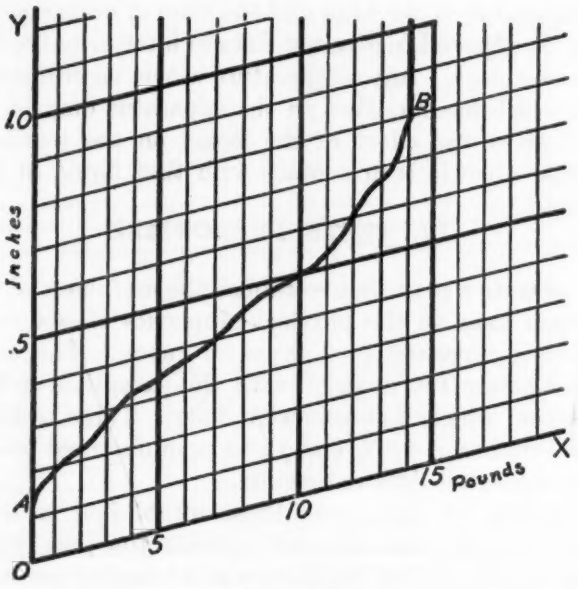

FIGURE 4

ing load may be read directly. It is the projection on the axis of X of the point B where the curve rises abruptly for the last time. (See fig. 4.) Rayon elongates upon wetting. This elongation of the yarn is the difference in the readings O and A on the axis of Y. O is the zero point and A is the point where the load is first applied to the fibers. The stretch at break is the difference in the readings A and the projection on the axis of Y of the point B. Let D represent the initial separation of the jaws. Then the per cent stretch of the wet yarn is given by the following formula:

$$\text{Per cent stretch} = \frac{B-A}{A+D} \times 100$$

[11] Samples are conditioned by exposing them to air having a definite temperature and humidity until the moisture content of the sample reaches equilibrium.

7. DISCUSSION OF APPARATUS AND PROCEDURE

This method, developed primarily for determining the stress-strain curves for rayon yarns, is applicable to all textile yarns and to any cloth. A special problem arises when the textile to be tested contracts when it comes in contact with water. This case can be handled by inserting the sample in the jaw in the regular way and then running the jaws of the machine close enough together so that there will be some slack in the textile after wetting. The test is made as usual, but corrections in calculations have to be made to compensate for the difference in procedure.

The temperature of the bath and the time of immersion are factors which may be adjusted to give test data of interest to the textile trade and to the consumer. Any temperature within an ordinary range and any liquid which has no effect on the apparatus may be used. The results will show the effect of the liquid on the tensile properties of the textile when it is in contact with that liquid at a particular temperature.

IV. TESTS PERFORMED

A series of tests was made to establish the usefulness of this method and to obtain data on the physical properties of wet rayons. The samples tested represent four types of rayon. The size of yarns was approximately 150 denier,[12] with the exception of the cuprammonium rayon, which was somewhat finer. These tests were made during the summer of 1927, and yarns manufactured at a later date might give somewhat different results.

The conditions of tests were those established in the multiple-strand test; namely, the distance between the jaws was 4 inches; the rate of separation of the jaws was 12 inches per minute; and 80 strands were broken for each test. All samples were conditioned at 65 per cent relative humidity and 20° C. before testing.

The following tests were made:

1. The samples were broken dry.
2. The samples were broken wet at room temperature, and at 60°, 70°, 80°, 90°, and 100° C.
3. The samples were wet one-half hour in water at room temperature, dried and broken.
4. The samples were wet in boiling water for one-half hour, dried and broken. The samples were first cooled in water before exposing to the air.

[12] The denier is the weight in grams of 9,000 meters of yarn.

Tables 1 and 2 and Figures 5 and 6 give the results of these tests. These results, and those of other investigators, show the weakening of rayon upon wetting. The temperature of the bath has little effect on the breaking strength of regenerated cellulose rayon. As the temperature of the water is increased, the wet breaking strength of the cellulose acetate rayon tested decreases, and its

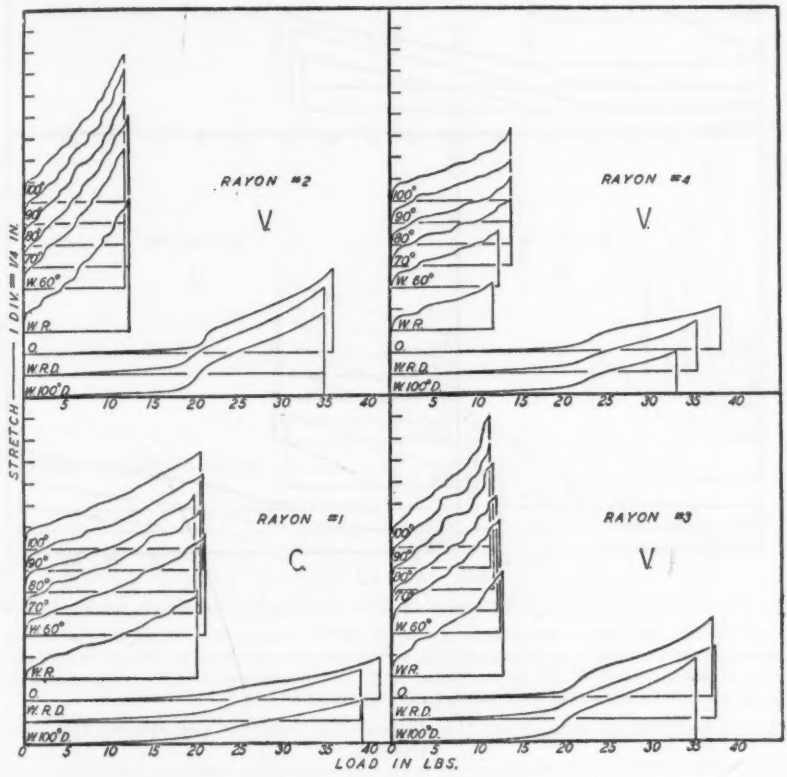

FIGURE 5.—*Stress-strain relations of rayons—multiple-strand tests on 80 strands*

W. 100° D., wet sample one-half hour in water at 100° C.; broken dry. *W. R. D.*, wet sample one-half hour in water at room temperature; broken dry. *O.*, broken dry. *W. R.*, broken wet at room temperature. *W. 60°*, broken wet at 60° C. *70°* broken wet at 70° C. *80°* broken wet at 80° C. *90°* ,broken wet at 90° C. *100°*, broken wet at 100° C.

NOTE.—Charts on Figures 5 and 6 have been replotted to rectangular coordinates, and in order to avoid confusion a different axis has been used for each curve.

NOTE.—Charts on Figures 5 and 6 have been replotted to rectangular coordinates, and in order to avoid confusion a different axis has been used for each curve.

elongation due to wetting and its stretch at break increase. Cellulose acetate rayon also shows definite changes in stress-strain relations when treated for one-half hour in boiling water and broken dry.

Work is now under way to explain these stress-strain relations, and also the peculiar behavior observed in cellulose acetate rayons.

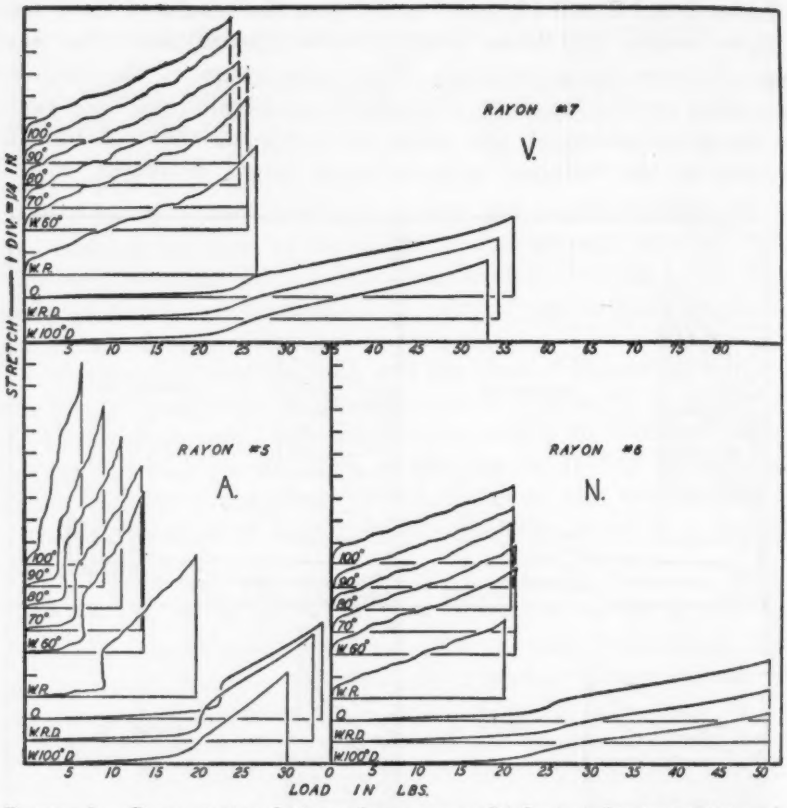

FIGURE 6.—*Stress-strain relations of rayons—multiple-strand tests on 80 strands*

W. 100° D., wet sample one-half hour in water at 100° C., broken dry. *W. R. D.*, wet sample one-half hour in water at room temperature; broken dry. *O.*, broken dry. *W. R.*, broken wet at room temperature. *W. 60°*, broken wet at 60° C. *70°*, broken wet at 70° C. *80°*, wet broken at 80° C. *90°*, broken wet at 90° C. *100°*, broken wet at 100° C.

TABLE 1.—*Effect of wetting on the stress-strain data for dry rayons (80 strands broken)*

Sample No.	Kind	Condition of test	Breaking strength	Stretch at break
			Pounds	*Per cent*
1	Cuprammonium (135 denier).	Original sample	40.5	12.3
		Wet ½ hour at room temperature, broken dry	38.5	14.3
		Wet ½ hour at 100° C., broken dry	38.5	14.5
2	Viscose (150 denier).	Original sample	35.5	24.3
		Wet ½ hour at room temperature, broken dry	34.7	25.0
		Wet ½ hour at 100° C., broken dry	34.5	24.3
3	Viscose (149 denier).	Original sample	37.0	20.8
		Wet ½ hour at room temperature, broken dry	37.0	20.5
		Wet ½ hour at 100° C., broken dry	35.2	23.5
4	Viscose (153 denier).	Original sample	37.5	13.0
		Wet ½ hour at room temperature, broken dry	38.7	15.0
		Wet ½ hour at 100° C., broken dry	37.8	15.3
5	Cellulose acetate (156 denier).	Original sample	34.0	27.0
		Wet ½ hour at room temperature, broken dry	34.7	29.3
		Wet ½ hour at 100° C., broken dry	30.5	26.3
6	Chardonnet [1] (154 denier).	Original sample	50.5	17.0
		Wet ½ hour at room temperature, broken dry	50.3	15.0
		Wet ½ hour at 100° C., broken dry	51.0	14.3
7	Viscose (159 denier).	Original sample	55.5	21.8
		Wet ½ hour at room temperature, broken dry	54.7	23.0
		Wet ½ hour at 100° C., broken dry	53.5	22.8

[1] Commonly called nitrocellulose rayon.

TABLE 2.—*Stress-strain data for wet rayons (80 strands broken)*

Sample No.	Kind	Temperature of bath	Breaking strength	Loss in breaking strength	Elongation due to wetting	Stretch at break [1]
		° C.	*Pounds*	*Per cent*	*Per cent*	*Per cent*
1	Cuprammonium (135 denier)	[2] 20–21	20.0	50.6	3.3	20.6
		60	20.7	48.9	4.3	26.9
		70	20.7	48.9	4.3	27.3
		80	20.3	49.9	4.3	23.7
		90	20.3	49.9	5.0	21.4
		100	19.8	51.2	5.3	22.3
2	Viscose (150 denier)	[2] 20–21	12.7	64.2	5.0	31.7
		60	12.2	65.6	5.8	32.7
		70	12.3	65.3	6.0	32.4
		80	12.0	66.2	6.0	30.8
		90	12.0	66.2	6.0	32.4
		100	12.2	65.3	6.3	30.4
3	Viscose (149 denier)	[2] 20–21	12.7	65.7	5.5	22.3
		60	12.3	66.7	6.3	25.2
		70	12.2	67.0	6.5	27.0
		80	11.7	68.4	6.8	27.2
		90	11.7	68.4	6.3	26.3
		100	11.5	68.9	6.5	29.1
4	Viscose (153 denier)	[2] 20–21	12.0	68.0	3.8	9.6
		60	12.7	66.1	4.3	12.2
		70	14.0	62.7	4.3	13.7
		80	13.8	63.2	4.3	13.9
		90	14.0	62.7	4.3	14.6
		100	14.0	62.7	4.3	15.8
5	Cellulose acetate (156 denier)	[2] 20–21	19.2	43.5	.8	40.2
		60	13.7	59.7	.8	43.7
		70	13.3	60.9	.8	42.9
		80	11.2	67.1	1.0	44.3
		90	8.2	75.9	1.5	48.0
		100	6.5	80.9	2.5	51.0
6	Chardonnet (154 denier)	[2] 20–21	20.8	58.8	3.0	19.2
		60	21.2	58.0	3.3	20.1
		70	21.3	57.8	3.0	20.4
		80	20.5	59.4	3.5	19.1
		90	20.7	59.0	3.3	19.1
		100	20.8	58.8	4.3	17.7
7	Viscose (159 denier)	[2] 20–21	26.5	52.3	3.8	31.8
		60	25.5	54.1	4.0	32.7
		70	25.7	53.7	4.0	32.4
		80	24.7	55.5	4.0	30.8
		90	24.3	56.2	4.0	32.4
		100	23.3	58.0	3.8	30.4

[1] This stretch at break does not include the elongation due to wetting.
[2] 20°–21° C. is room temperature.

V. SUMMARY

A method for determining the stress-strain relations of textiles when wet has been developed. With this method measurements can be made as accurately as those obtained with the multiple-strand test for dry yarns.[13] The apparatus is so designed that a test may be made over a range of temperatures. The method may be used for all types of textiles, either as yarn or fabrics.

Results are given which show the effect of water at various temperatures on the stress-strain relations of rayons.

[13] "The average deviations in the strength results of the multiple-strand method seem to be within the sensitivity of the machine (one-half pound); the stretch variations are about three times the possible experimental error caused by the machine." C. W. Schoffstall and H. A. Hamm, B. S. Jour. Research, 2, p. 879; 1929.

VI. ACKNOWLEDGMENTS

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CORROSION OF OPEN-VALLEY FLASHINGS

By K. Hilding Beij

ABSTRACT

In recent years some trouble has been caused by corrosion of copper flashings, particularly of open-valley flashings on buildings with shingle roofs. Sixteen-ounce copper may be perforated in 15 to 20 years under severe conditions of service. Failures have been found in a few localities only. They seem to be more frequent in New York City and its environs than elsewhere in the Eastern and Central States. One case from Washington, D. C., is significant for here the corrosion occurred where one sheet of copper overlapped another.

The corrosion, for convenience called line corrosion, results in a narrow line of holes or cracks immediately under the edge of the overlying roofing. It appears to be an accelerated attack due to differential aeration of the water retained by capillarity between the roofing and the flashing after a rainfall. This water is shielded from the air except along the edge of the roofing where it is freely exposed.

Accelerated corrosion tests showed that a solution containing both sulphur dioxide and sodium chloride produced rapid line corrosion. Solutions of either alone produced no visible line corrosion in the same length of time. This result suggests that under ordinary conditions line corrosion will be found only in cities near the seacoast. The rate of corrosion depends in large measure on the roofing material. A porous, absorbent roofing, such as wood shingles, holds more water in contact with the flashing after a rainfall and dries out more slowly than a relatively impervious material like slate. Hence, more rapid corrosion takes place.

The laboratory tests indicate that a simple and inexpensive modification in construction will eliminate troubles due to line corrosion. This modification consists of the insertion of a smoothly finished hardwood strip between the roofing and the flashing. The strip should be placed about an inch back of the edge of the roofing and nailed firmly and tightly to the flashing. In the accelerated tests, specimens made in this way were unaffected by more than three times the test exposure which caused line corrosion failure of specimens without the strip. It is reasonable to believe that a similar difference will be found under service conditions. If so, then no appreciable line corrosion would occur with the modified construction in 50 years or more even under conditions as severe as those in New York City and its environs.

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I. INTRODUCTION

For several years the Bureau of Standards and the Copper and Brass Research Association have been conducting a joint investigation of problems concerning copper roofing, the chief object of the investi-

gation being to increase the usefulness of copper as a building material. One of these problems was the peculiar form of localized corrosion which sometimes occurs in sheet copper when used for the flashing of open valleys, According to all available information, copper flashings very rarely fail by corrosion and such failures appear to be confined to a few localities. However, copper is a material whose use for roofing purposes is based on its well recognized resistance to destructive atmospheric agencies. Therefore, any factor which tends to limit the life of copper roofing, even to a slight degree, is of far greater import than it would be for a cheaper material not selected primarily for long life.

The purpose of the investigation discussed in this paper was to discover the causes of the corrosion of valley flashings and to find some

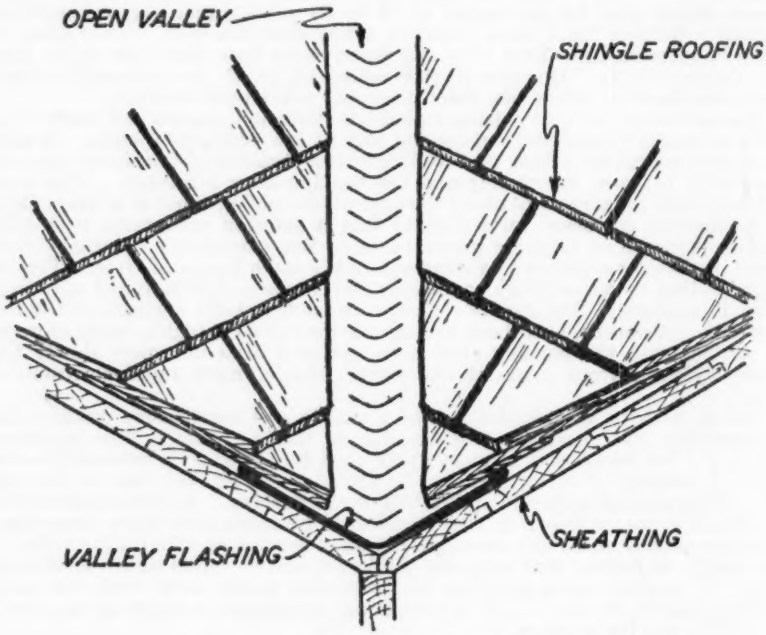

FIGURE 1.—*Diagram of an open valley*

means for eliminating them, so that the service life of a roof will not be limited by the life of the flashing. Further, it is important to be able to recognize the circumstances under which such corrosion is likely to be serious enough to warrant precautionary measures. In order to attain these ends it was necessary to develop an accelerated test which would reproduce actual conditions as nearly as possible.

For convenience, some of the terms used in this paper are defined. *Roofing* denotes the material which covers the major portion of the roof of a building. *Flashing* is sheet metal applied on various parts of the roof to ensure protection against leakage. When two sloping roof surfaces intersect in a reentrant angle, the trough thus formed is called a *valley*. If the roofing is continuous through the valley, the valley is *closed;* whereas if the roofing is not continuous, leaving a channel in the bottom of the valley, the valley is called *open*. The

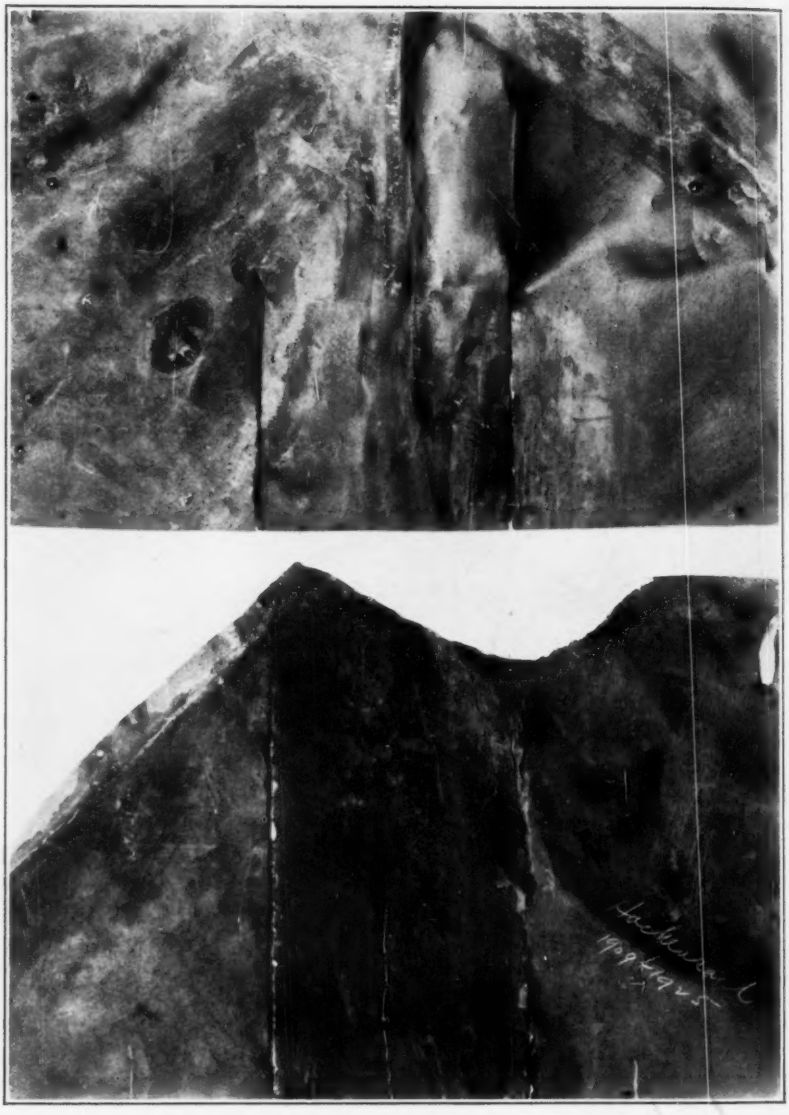

FIGURE 2.—*Sections of an open-valley flashing which had failed in service*

Approximately one-fourth size.

channel of an open valley is lined with sheet metal which extends up under the roofing on each side and this lining is the *valley flashing*. Figure 1 shows the essential features of an open valley where the flashing is applied in the usual manner.

The term *line corrosion* is used to designate localized corrosion occurring in a narrow band from 1/32 to 3/32 inch wide in the flashing located under the very edge of the overlying roofing.

II. FLASHING FAILURES

Sections of a valley flashing which had failed in service are illustrated in Figure 2. These specimens were removed from a residence in Hackensack, N. J., about 16 years after the construction of the building. The roofing was "Creo-dipt" shingles and the flashing was 16-ounce Roofing Temper (soft) copper (16 ounces per square foot, 0.0216 inch nominal thickness). This example is typical of other failures except that in most cases repairs are made as soon as the flashing has been penetrated at any point and before the continuous crack has been formed.

The upper specimen in the photograph shows the appearance of the under surface of the flashing. Note the extreme localization of the corrosion, which has penetrated the copper in two very narrow bands 1/16 to 3/32 inch wide, and the very good condition of the copper elsewhere.

The lower specimen in the photograph, taken from another position in the same valley, shows the upper surface of the flashing. The central darker portion, which is about 5 inches wide, formed the open part of the valley. The dark and rough appearance of this part is due to paint applied in an effort to stop the corrosion. The two side portions of the specimen were the parts covered by the overlying shingles. The copper was evidently in perfect condition save for the two cracks located along the edge of the overlying shingle roofing.

In practically all of the cases for which definite information is available the roofing was of wood shingles. This has led to the opinion, held by many sheet-metal workers and others interested, that chemical action due to the wood shingles is directly responsible for the corrosion of valley flashings. However, an example very similar in appearance to the valley-flashing failures was found in Washington, D. C., where no wood shingles were present. The corrosion occurred on a 3-inch stack used to carry off hot gases and fumes from two gas heaters. At each joint of the stack, where one section overlapped another, narrow grooves and cracks were found. These cracks were so strikingly similar in their appearance and their location under the edge of the overlapping section to the failures in the valley flashings, such as that shown in Figure 2, as to lead to the conviction that the same causes were operating. Service conditions were exceptionally severe and it was necessary to replace the stack after about 12 years.

Failures of valley flashings are not a common occurrence. Inquiries throughout a large part of the Eastern and Central States have shown that in most localities they are unknown. Actual examples of failures have been found in a limited area around New York City, and in Philadelphia and Erie, Pa. In the area around New York City,

including western Long Island and, in particular, the Passaic Valley of New Jersey, valley corrosion appears to be more of a problem than elsewhere.

The information on this subject is so meager that no conclusions can be drawn regarding the relation between failures and their location with respect to railroads or factories, orientation and exposure of roof, and other factors which might possibly be of significance. It should be mentioned, however, that on several of the specimens received for examination, the roofing shingles were almost black with soot and cinders from coal smoke.

III. EXPERIMENTAL WORK

1. FIRST SERIES OF TESTS

The test specimens were furnished by the Copper and Brass Research Association. These consisted of sample roofs about 30

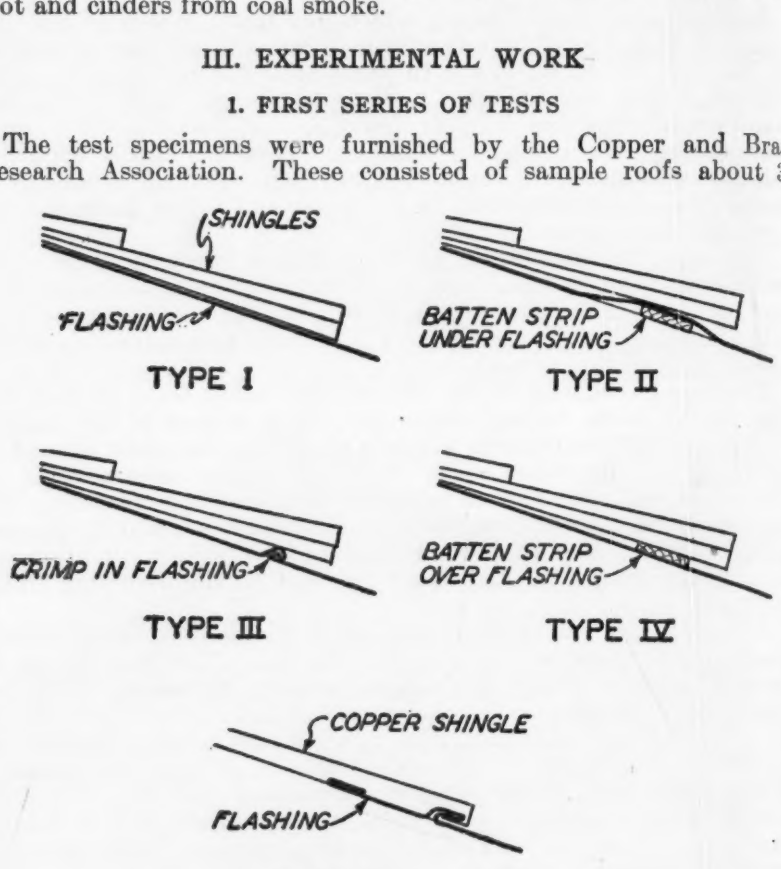

FIGURE 3.—*Types of construction for open-valley flashings*

inches square mounted on a 1 to 3 pitch, (1 inch rise for each 3 inches horizontal). The flashing was placed along the lower edge of each specimen. This flashing was commercial, (electrolytic), sheet copper of 16-ounce gage, which corresponds to a nominal thickness of 0.0216 inch. This gage is the one most commonly used for roofing purposes. Soft copper (Roofing Temper) was used on all specimens except No. 2, which was flashed with hard (Cornice Temper) copper. A descriptive list of the specimens is given in Table 1 and diagrams of the various methods of construction in Figure 3. Figure 4, a photo-

graph taken while tests were in progress, gives a clear idea of the appearance of the specimens.

The solutions were supplied from a large copper-lined tank shown to the left of Figure 4. From the tank extended two perforated brass pipes, one over each row of specimens just forward of the back edges of the specimens. By this arrangement, solution was distributed evenly over the entire width of the specimens and flowed over practically all of the roofing before striking the flashing. By placing copper wires in the holes of the pipes and adjusting the gradients, very nearly the same flow was obtained over each specimen. The composition of the solutions was approximately as given later, but no attempts were made to obtain great accuracy. The metal of the distributing system was, of course, attacked and this changed the composition of the solution somewhat before it reached the specimens. However, since all of the specimens received very nearly the same treatment, intercomparisons are valid. Apparatus and specimens were thoroughly cleaned weekly, and oftener if it seemed necessary. A series of five tests was made, all on the same set of specimens.

The complete operation of wetting a specimen by running solution over it, together with the subsequent period of drying, will be called one cycle.

Test No. 1.—Tap water was run over the specimens continuously for seven hours each day (except Sundays). The total amount of water in the system was 36 gallons; this was recirculated at a rate of approximately 1 gallon per minute per specimen. After 16 cycles, which took about three weeks, it was evident that no line corrosion was taking place, at least at a rate warranting continuance of this procedure.

Test No. 2.—The solution was not recirculated in this or in the subsequent tests of the series.

A 0.4 per cent solution of sulphur dioxide was used. The cycle consisted of a 2-hour period during which the solution was dripping on the specimens, followed by a period of 22 hours for drying. The rate at which the solution was supplied was about 0.3 gallon per specimen per minute. After 34 cycles it was clear that this solution was too weak to bring any results within a reasonable time. Furthermore, it seemed that much shorter cycles could be used to advantage, as more drying-out periods would be obtained in the same length of time. Accordingly, the apparatus was modified so that solution could be run for 3-minute periods at 3-hour intervals.[1] Solution was supplied at the rate of about 0.25 gallon per cycle per specimen. This procedure was followed in all of the remaining tests of the series.

Test No. 3.—In this test a 2 per cent solution of sulphur dioxide was used. Five or six 3-hour cycles were run five nights each week. No traces of line corrosion could be observed after 192 cycles over a period of about two months.

Test No. 4.—A normal solution, 5.65 per cent, of sodium chloride was used. No definite indications of line corrosion could be detected after 93 cycles in about five weeks.

[1] An apparatus which would function automatically at night was necessary. A rubber stopper, fitted to the outlet at the bottom of the solution tank, was operated by a rod passing up through the tank to a cam rotated by weights. A pin on the cam shaft, corresponding to the closed position of the stopper, was checked by the plunger of an electromagnet. Current through the electromagnet moved the plunger, thus releasing the check pin. After one-half turn of the cam, a second pin, corresponding to the open position of the stopper, was checked against the plunger. When the current was cut off, the cam made another half turn to the initial position. The operation of the electromagnet was controlled through a relay by a timing device. This consisted of an ordinary alarm clock with wire brushes soldered to the hands. Four contact points for the hour hand, placed equidistant on the clock face, were connected to one side of the relay and a single contact point for the minute hand to the other side. The electomagnet operated every three hours when the hour and minute hands made contact simultaneously.

Test No. 5.—The solution was a mixture containing 2 per cent sulphur dioxide and 5.65 per cent sodium chloride. Line corrosion began to be evident almost immediately. This test was continued until all of the specimens had failed. The number of cycles in test No. 5 required for each of the specimens to reach the failure point is reported in Table 1.

TABLE 1.—*Descriptive list of specimens and summary of results of first series of tests*

Specimen No.	Type of construction [1]	Flashing temper [2]	Roofing material	Cycles for failure	Remarks
1	I	R. T.	Red cedar shingles	93	Line corrosion failure.
2	I	C. T.	do	50	Do.
3	I	R. T.	Cypress shingles	99	Do.
4	II	R. T.	Red cedar shingles		Line corrosion failure; time not observed.
5	III	R. T.	do		Do.
6	I	R. T.	"Creo-dipt" shingles (color green).	93	Line corrosion failure.
7	IV	R. T.	Slate	187	Line corrosion failure, at edge of lath.
8	I	R. T.	Asbestos shingles	255	Line corrosion failure.
9	IV	R. T.	Terra cotta Spanish tile	193	Line corrosion failure, at edge of lath.
10	V	R. T.	Copper shingles (9-ounce C. T.).	(93)	Copper shingles failed. No line corrosion.

[1] See Figure 3.
[2] R. T. signifies Roofing Temper (soft) copper. C. T. signifies Cornice Temper (hard) copper. All specimens on pitch of 1:3 (rise of 1 inch to every 3 inches horizontal).

2. RESULTS OF THE FIRST SERIES OF TESTS

During the first test, the water became very strongly impregnated with materials leached out of the shingles. The effect of this solution on the copper was hardly noticeable. At the end of the fourth test, no line corrosion could be observed, in spite of the fact that during all of this time the flashings were exposed to solutions which had run over and soaked through the wood shingles. The evidence indicates that chemical action induced by wood shingles is not a factor of importance in the corrosion of valley flashings. Indeed, if this were the case, failures of valley flashings would be far more common and not restricted to certain localities.

On the other hand, the solution used in test No. 5, a mixture containing sulphur dioxide and sodium chloride, produced very rapid line corrosion. This result seems to account for the fact that most of the known failures have been found in New York City and its environs where the air is contaminated by coal smoke and also carries considerable salt on account of its nearness to the ocean. That no failures have been found in inland cities would then be explained by the very much slower rate of corrosion when sulphur dioxide alone is involved.

In order to make intercomparisons among the specimens it is necessary to adopt some criterion for failure and some means for measuring the endurance or life of a specimen under test. Complete penetration of the flashing at any point under the edge of the overlying roofing, where line corrosion would be expected to occur, was assumed to represent failure of the specimen. In the case of specimens of Type III construction (see fig. 3), complete penetration of the upper layer of copper on the crimp was considered failure. In the first series of tests, the failure of specimens Nos. 4 and 5 could not be observed, as the roofing was not removable. The test life of a specimen was taken as the number of cycles with the sulphur dioxide-

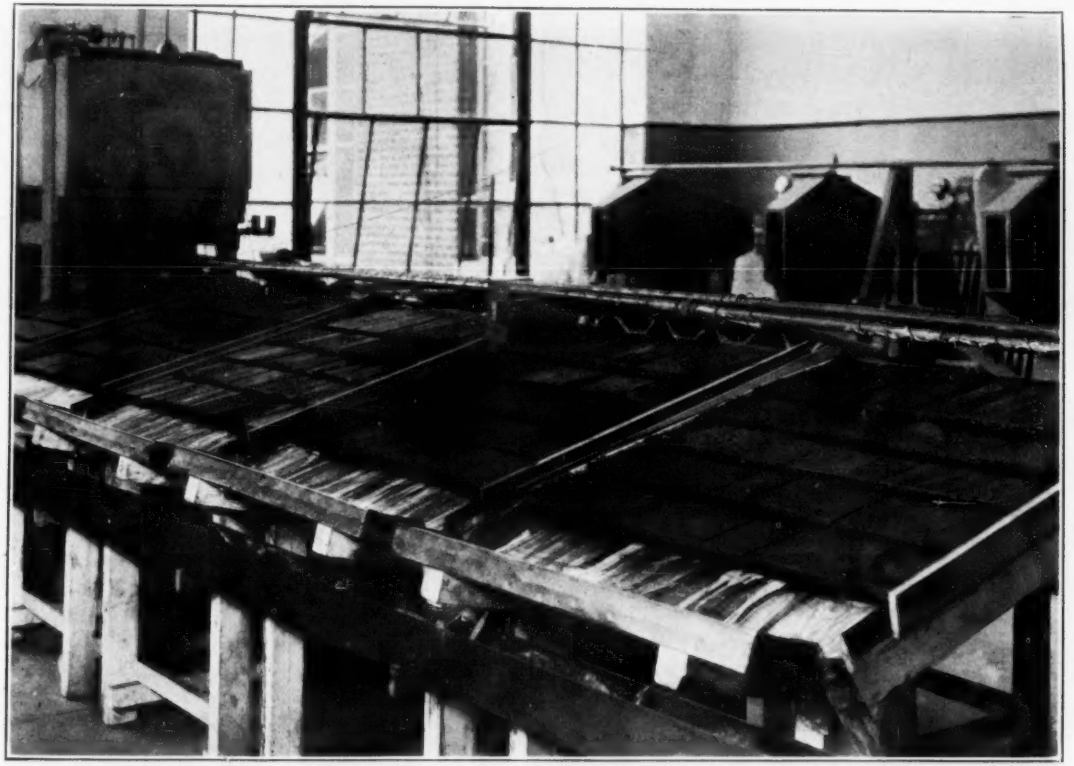

FIGURE 4.—*First series of tests of open-valley flashings, apparatus, and specimens*

FIGURE 6.—*Specimen No. 2 after test*

Arrows point to line corrosion.

sodium chloride solution required to cause failure. Although other solutions were used in the first series, the line corrosion produced by them could not be detected and was therefore assumed to be negligible. A summary of the results is given in Table 1, and shown graphically in Figure 5. The results for 3 of the 10 specimens are not included in Figure 5 for reasons which will appear later.

The first failure occurred on specimen No. 2, shown in Figure 6. The shingles have been removed and the lower (double) course has

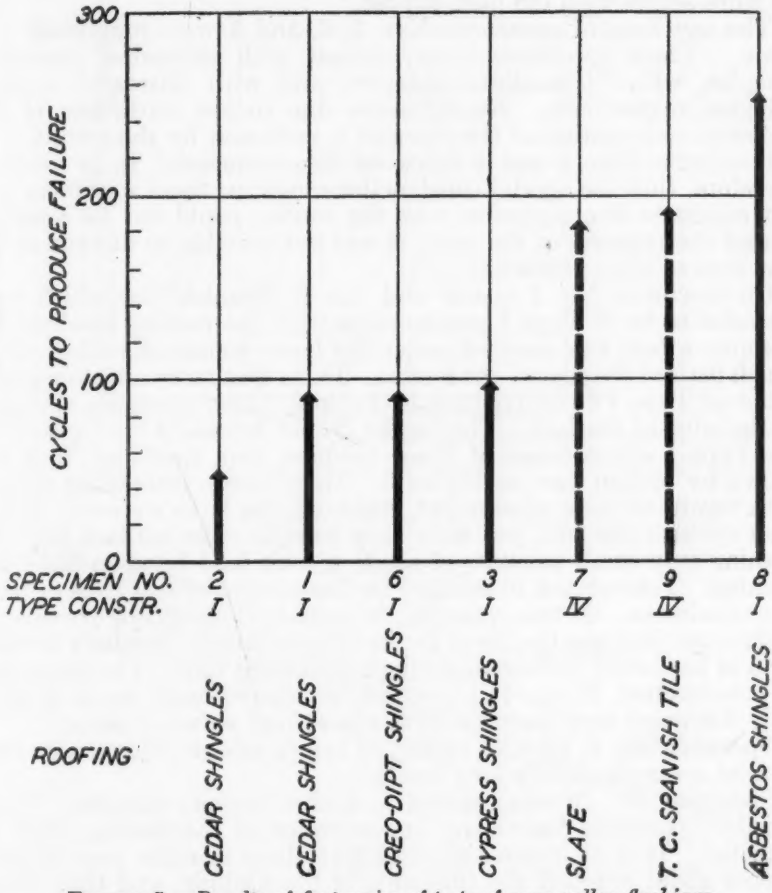

FIGURE 5.—*Results of first series of tests of open-valley flashings*

16-ounce Cornice Temper (hard) copper on specimen No. 2; 16-ounce Roofing Temper (soft) copper on all other specimens. The broken lines indicate that the roofing on these specimens was separated from the flashing by a lath at the edge of which line corrosion occurred.

been separated and replaced a few inches above its original position. The line corrosion shows as a well-defined line (marked by the arrows) running across the specimen. (All along the line was a deep groove which does not show well in the reproduction.) Careful inspection of the photograph will disclose, in addition, a number of holes at various points. At several points the line corrosion extends up along the sides of the shingles for an inch or more. The failure is typical of those which occurred on the other specimens.

Specimens Nos. 1 and 2 were similar in all respects save that soft copper (Roofing Temper) flashing was used on the first and hard (Cornice Temper) on the second. The hard copper is practically never used for flashing purposes. Specimen No. 2 failed after 50 applications of the mixed solution, while No. 1 required 93 applications for failure. Although results from tests employing only one specimen of a kind can not be considered as entirely conclusive, yet they strongly indicate that no advantage would be gained by substituting hard for soft copper. In fact, line corrosion would probably be more severe with the hard copper.

The test lives of specimens Nos. 1, 6, and 3 were practically the same. These specimens were covered with untreated red-cedar shingles, with "Creo-dipt" shingles, and with untreated cypress shingles, respectively. No difference due to any variations of the chemical composition of the shingles is indicated by the results.

Specimens Nos. 4 and 5 failed by line corrosion. It is evident, therefore, that the special constructions used on these specimens will not eliminate line corrosion. As the roofing could not be removed during the progress of the tests, it was not possible to determine the test lives of these specimens.

On specimens No. 7 (slate) and No. 9 (Spanish tile), which were intended to be of Type I construction with the roofing touching the flashing, a lath was inserted under the lower course of roofing about 1 inch back of the edge of the roofing. These specimens are accordingly listed as Type IV construction in Table I. Line corrosion appeared at the edge of the lath. The results do not represent true values for the Type I construction of these roofings, and, therefore, they are shown by broken lines in Figure 5. There is one interesting feature with regard to these specimens. Although the laths were wet during each cycle of the test, yet since they were in close contact with the flashing only small amounts of solution were held between laths and flashing. This seemed to account for the prolonged test lives of these two specimens. If this reasoning is correct, it should be possible to still further increase the life of the flashing by using a carefully finished strip of hardwood instead of a rough unfinished lath. The same type of construction (Type IV) applied to wood-shingle roofs is more fully discussed in connection with the second series of tests.

Specimen No. 8, with its roofing of heavy asbestos shingles or tiles, showed a comparatively long test life.

Specimen No. 10 was covered with sheet-copper shingles. These failed by corrosion before any line corrosion of the flashing could be detected. It is of interest to note that these shingles were of hard copper about one-half the thickness of the flashing, and that failure first occurred at bends and corners.

In Figure 5 the specimens, reading from left to right, are arranged in order of increasing test life. It is significant that this is also the order of the specimens when arranged according to the rate of drying from those drying most slowly on the left to those drying most rapidly on the right. Specimens Nos. 1, 2, and 6 dried very slowly, all at about the same rate. No. 3 dried noticeably faster, and Nos. 7, 8, and 9 quite rapidly. A relation between rate of drying and test life is suggested, but no definite conclusions can be based on this small number of specimens.

3. SECOND SERIES OF TESTS

The results of the first series of tests were inconclusive in several respects. In particular, the two special forms of construction (Types

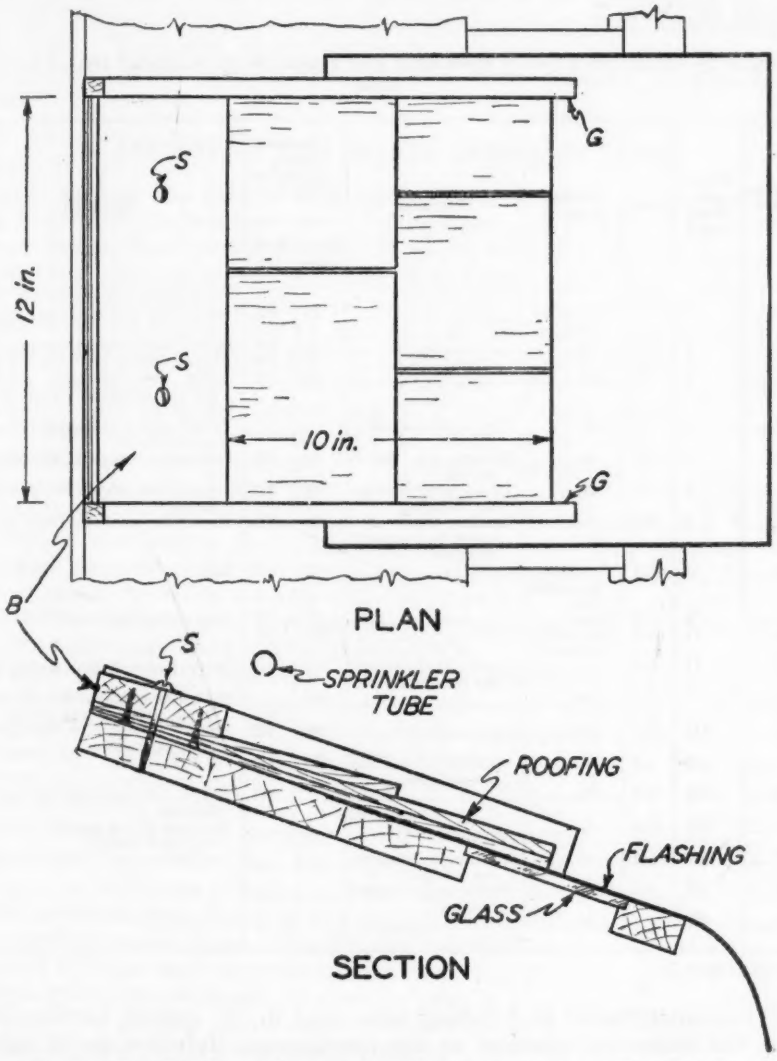

FIGURE 7.—*Specimens for second series of tests of open-valley flashings*

The roofing is fastened to the block *B* and the side guards *G*. This assembly is held in place by the removable screws S.

II and III) did not prove to be immune to line corrosion. Accordingly, a second series was undertaken.

Sketches showing a typical specimen are given in Figure 7. The flashing was nailed to the supporting stand. The glass window in the top of the stand made it possible to detect the first penetration of the flashing. The roofing was attached to a wood block (*B* in fig. 7)

and to two guard strips, *G*, which prevented overflow of solution along the sides of the specimen. This assembly was attached to the stand by two screws, *S*. Thus the roofing could be easily removed for inspection of the flashing and could be replaced in its original position and fixed by means of the screws. A descriptive list of the specimens is given in Table 2.

TABLE 2.—*Descriptive list of specimens and summary of results of second series of tests*

Specimen No.	Type construction [1]	Pitch	Roofing material	Remarks	Line corrosion, number of cycles to—		Remarks
					First trace	Failure	
11	I	1:3	Red cedar shingles.		22	138	Severe line corrosion, one crack.
12	I	1:2	do		22	220	Severe line corrosion, several cracks.
13	I	2:3	do		22	272	Line corrosion, several small holes.
14	I	1:1	do		71	148	Slight line corrosion, patch of severe corrosion with several holes.
15	I	1:3	do	For continuous drip			Failed after 1,152 hours of continuous drip.
16	I	1:3	do	Heater, for rapid drying.	22	138	Severe line corrosion, several holes.
17	I	1:3	do	Flashing painted under shingles.	31	242	Severe line corrosion, one small hole.
18	I	1:3	do	Roofing paper between flashing and shingles.	31	220	Severe line corrosion, one crack.
19	I	1:3	Composition shingles.		31	158	Slight line corrosion, one hole.
20	I	1:3	Slate		22	287	Line corrosion, several holes.
21	II	1:3	Red cedar shingles.		242	401	Do.
22	II	1:3	do	Flashing painted under shingles.	242	401	Severe line corrosion, several holes.
23	II	1:1	do		401		No failure at end of test, 475 cycles. Small patch deeply pitted.
24	III	1:3	do		138	242	Deeply pitted, hole through first layer of flashing.
25	III	1:3	do	Flashing painted under shingles.	242	373	Do.
26	III	1:1	do			242	Pitted, hole through first layer of flashing.
27	IV	1:3	do				No trace of line corrosion at end of test, 475 cycles.
28	IV	1:3	do	Flashing painted under shingles.			Do.
29	IV	1:3	do	Batten strip waterproofed.			Do.
30	IV	1:1	do				Do.

[1] See Figure 3.

Glass receptacles and tubing were used in the system for distributing the corrosive solution to the specimens. Joints were of rubber tubing. By adjustment of the sprinkler tubes a fairly uniform flow was obtained over each specimen. This flow was checked occasionally by measuring the run-off from the specimens. About one-tenth of a gallon of solution was required to thoroughly wet a specimen, and the flow was adjusted to give approximately this amount in six minutes.[2]

[2] The arrangement for starting and stopping the flow automatically was the same as that used in the first series of tests, except that a hard-rubber valve, with its stem on the cam shaft, was substituted for the stopper and cam combination.

The corrosive solution was the same as that used in the final test of the first series, namely, a mixture containing about 5.85 per cent of sodium chloride and 2 per cent of sulphur dioxide. As before, this mixture gave rapid results. It was intended to run six 3-hour cycles each night. However, this did not always allow the specimens to dry out thoroughly, especially during rainy weather when the humidity was high. Therefore, the schedule was varied at times to suit circumstances. Specimens and apparatus were cleaned at intervals as seemed necessary.

4. RESULTS OF THE SECOND SERIES OF TESTS

A résumé of the results is given in Table 2 and the comparative test lives of the specimens are shown graphically in Figure 8. Note in particular, that specimens Nos. 27 to 30, inclusive, showed no signs of line corrosion at the completion of the test. Although specimen No. 13 had not failed at the end of the test, pitting had progressed almost through the flashing at one point so that failure was imminent.

The action of different roofing materials is well shown by comparing specimens No. 11 (wood shingles), No. 19 (composition shingles), and No. 20 (slate), all of Type I construction. All of these failed by line corrosion, and, as nearly as could be judged by inspection, the total amount of corrosion was about the same in each case. However, the slate specimen (No. 20) which had the least porous or absorbent roofing and, therefore, dried out most rapidly in each cycle, had the longest test life. The composition shingles (No. 19) dried out more slowly than the slate, thus holding a film of water between roofing and flashings for a longer period each time. The failure was correspondingly hastened and the test life considerably shortened. The shingles (No. 11) were quite porous and absorbent, dried out very slowly, and retained liquid in contact with the flashing for a longer time than the other materials. Hence, as anticipated, the test life here is the shortest of all. The effect of the roofing material as regards line corrosion appears to be almost entirely dependent on the length of time which the material can hold solution in contact with the flashing. The more porous and absorbent the material, the shorter will be the test life of the specimen. Accordingly, specimen No. 18, which had a sheet of roofing paper inserted between the shingles and the flashing, should have a test life somewhere between those of the composition shingles and the slate. The roofing paper fitted more closely to the flashing than the composition shingles and, therefore, held back less liquid, so that drying was somewhat more rapid. As can be seen in Figure 8, the test life of specimen No. 18 falls about midway between those of the composition shingles (No. 19) and the slate (No. 20).

It is concluded, on the basis of the results of both series of tests, that wood shingles are not the primary cause of line corrosion, and that practically the only influence of the roofing material on line corrosion depends on its ability to retain water in contact with the flashing. This conclusion is borne out by the data relating to failures of valley flashings. These data show that line corrosion may occur in the absence of any material other than the copper itself. Moreover, failures appear to be restricted to certain localities. They do not occur generally in all places where wood shingles are used.

If this conclusion is correct, then a specimen mounted on a steep pitch should have a longer test life than a similar specimen with only a slight pitch. For, as the pitch or slope of the roof is increased, water will drain off more completely and less will be retained between

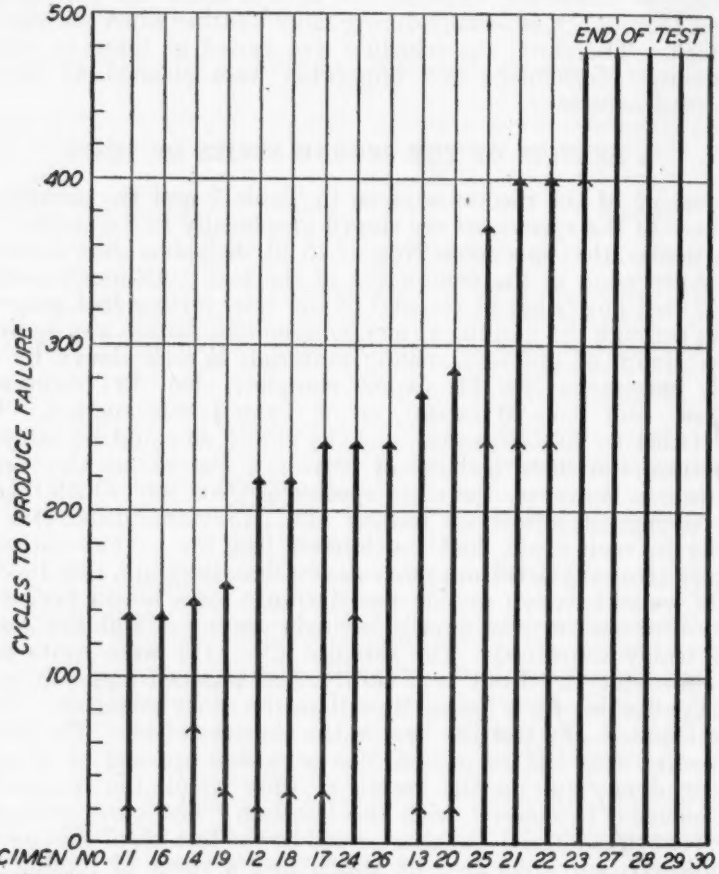
500
400
300
200
100
0
CYCLES TO PRODUCE FAILURE
END OF TEST
SPECIMEN NO. 11 16 14 19 12 18 17 24 26 13 20 25 21 22 23 27 28 29 30
TYPE CONSTR. I I I I I I I III III I I III II II II IV IV IV IV
ROOF PITCH 1/3 1/3 1/3 1/3 1/2 1/3 1/3 1/3 1/1 2/3 1/3 1/3 1/3 1/3 1/1 1/3 1/3 1/3 1/1
ROOFING ON SPEC. NO. 19 - COMPOSITION SHINGLES
ON SPEC. NO. 20 - SLATE
ON ALL OTHERS - RED CEDAR SHINGLES

FIGURE 8.—*Results of second series of tests of open-valley flashings*

First (light) arrowhead represents first noticed trace of line corrosion. Second (heavy) arrowhead represents failure. All flashings of 16-ounce Roofing Temper (soft) copper.

the roofing and the flashing. Comparing specimens Nos. 11 to 14, inclusive, all of wood shingles but with progressively increasing pitch, it is found that the test life increases as the pitch increases. No. 14 is an apparent contradiction. However, although failure occurred very early on this specimen, severe line corrosion was limited to a small area and most of the specimen was in fairly good condition. It is believed that if some better way of measuring the total amount

of line corrosion were feasible, this specimen would not be so far out of place with respect to the others. Reduced corrosion on specimens of steeper pitch was also found for other forms of construction—as may be seen by comparing the results for specimens Nos. 21 and 23, and also for specimens Nos. 24 and 26. It is true that specimen No. 26 failed at about the same time as specimen No. 24, but the total amount of corrosion over the whole specimen was considerably less.

The attempt was made to determine directly the effect of drying. Specimen No. 16 was provided with an electric heater which accelerated drying. However, the specimen failed at the same time as No. 11, which was allowed to dry without artificial aid. The question arises as to whether the retarding effect of the more rapid drying may not have been overcome by an accelerating effect due to the much higher temperature. Specimen No. 15, which was kept continuously wet except for one day each week, did not fail by definite line corrosion. Careful examination of this specimen while the test was in progress showed that the liquid between the flashing and the roofing was in continual motion. This motion was due to the slow steady flow of solution required to keep the specimen wet. On the specimens periodically wetted and then allowed to dry slowly the solution between roofing and flashing was in a quiet and undisturbed state during the period of drying. The test conditions were not the same in both cases, so that no comparisons of the results are made.

Three possible methods of counteracting line corrosion were studied. These were painting of the flashing, separation of flashing and roofing by building paper, and variations in construction.

The flashing on one specimen of each type of construction was painted with a heavy coat of red lead paint. The painting covered all of the flashing under the roofing and extended about one-half inch beyond the edges of the roofing. No comparison can be made for Type IV construction, since neither painted nor unpainted specimens showed any trace of line corrosion at the conclusion of the test. The unpainted (No. 21) and the painted (No. 22) specimens of Type II construction failed at the same time. On Types I and III the painted specimens showed somewhat increased test life. (Compare No. 17 with No. 11 and No. 25 with No. 24.) The painting apparently has some retarding effect, but not enough to warrant its use as a protective agent.

A sheet of building paper between shingles and flashing increases the test life, as previously mentioned, but not enough to make this expedient of any great value.

A number of intercomparisons are possible for the four types of construction tested. (See fig. 3.) Taking first the specimens Nos. 11, 21, 24, and 27, all with wood-shingle roofing on 1 to 3 slope, it is found that in order of increasing test life the types of construction are I, III, II, IV. Taking next the specimens with painted flashings (Nos. 17, 22, 25, and 28) we get the same order. Finally for the set of specimens on a steep slope (1 to 1 pitch, specimens Nos. 14, 23, 26, and 30) we find the types of construction again ranked in the same order.

The usual form of construction (Type I) thus appears to be the most susceptible to line corrosion. Type III construction, with a crimp in the copper which supports and raises the lower course of roofing, is a considerable improvement, though much inferior to the remaining two types.

While it does not offer complete protection, the Type II construction has certain advantages which may make its use desirable with with nonabsorbent roofings like slate or under conditions of service not highly conducive to line corrosion. In the first place, the flashing may be secured by cleats as is the usual practice. Secondly, the batten strips may be placed by the carpenter before the sheet-metal man starts his work. Finally, there is no obstruction to the flow of any water which might seep through the shingles just above the batten strip. Also it might be added that any strips of wood of the right dimensions, such as laths, may be used as batten strips without special preparation. Since sharp bends are undesirable, the proper laying of the flashing is important.

None of the specimens (Nos. 27 to 30, inclusive) of Type IV construction showed any signs of line corrosion at the end of the test. This type of construction then should prevent line corrosion, or at least retard it to such an extent as not to limit the useful life of the roof. The value of this form of construction is dependent on three considerations. First, only a very small fraction of the water falling on the roof can ever reach the junction between the batten strip and the flashing. Second, the batten strip is in close contact with the flashing and therefore little, if any, water can penetrate between the strip and the flashing. And third, if the strip is of hard, dense wood or is thoroughly waterproofed and has smooth surfaces, it will not hold water by capillarity to any appreciable extent. The strip then tends to prevent the formation of a slowly drying film of water such as causes line corrosion.

In the absence of data to the contrary, it is reasonable to believe that the life of a flashing under actual service conditions on a roof will be directly proportional to its test life. The line corrosion produced by 138 test cycles on specimen No. 1, Type I construction, was about the same in amount as that which is produced in 15 years or more on a roof under the most severe conditions. Therefore if Type IV construction, which was unaffected by 475 test cycles, were used on a roof, the flashing would probably show no signs of line corrosion for 50 years or more.

IV. DISCUSSION OF LINE CORROSION

The localized intense corrosion, which we have called line corrosion, is an interesting case of the type of attack occurring with differential aeration. Figure 9 is a diagram showing, on a large scale, approximately the relation between roofing, flashing, and retained liquid and the location of the line corrosion. It will be observed that the line corrosion is very close to the edge of the roofing, but definitely back of it. This has been checked on all the test specimens and on four available service specimens. We have then a layer of liquid containing corrosive agents in contact with the flashing, part of the layer being exposed freely to the air and part being shielded by the overlying roofing. The corrosion of the flashing takes place near the region of separation between aerated and nonaerated portions of the solution, but under the nonaerated portion.

Evans [3] has shown that, in general, when a metal is exposed to a solution, part of which is aerated and part nonaerated, the metal

[3] U. R. Evans, Corrosion of Metals, Arnold & Co. (2d ed.); 1926. Also, Corrosion of Copper and Copper Alloys, J. Soc. Chem. Ind., **43**, p. 127T; 1924.

under the nonaerated portion will be anodic to that under the aerated portion and will be corroded. If the aeration is accompanied by agitation, such as stirring, copper is an exception to the general rule and the part of the metal under the aerated portion corrodes. However, if differential aeration can be secured without stirring, then copper will behave as other metals and the corrosion will take place on the nonaerated part.

After a rainfall water containing dissolved impurities is retained on a valley flashing for some time in a quiescent state, approximately as shown in Figure 9. Near the solution-air interface there will be a very narrow cathodic area on the flashing under the aerated portion of the solution. Adjacent to this (under the roofing) will be a relatively wide anodic area under the nonaerated portion of the solution. The current density over the anodic area will be a maximum along a narrow band close to the cathodic area, decreasing very rapidly to extremely low values farther away from the cathodic area. Hence, practically all of the corrosion will be concentrated in a narrow band under the very edge of the roofing.

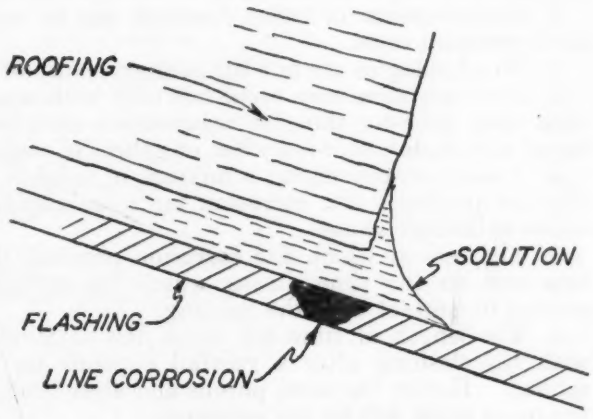

FIGURE 9.—*Diagram of open-valley flashing to illustrate manner in which line corrosion occurs*

Further studies would be required to work out the reactions which take place with the various solutions. In the tests no account was taken of carbon dioxide or other possible factors which may have been present and certainly would be involved under service conditions. With the sulphur dioxide-sodium chloride solution, which produced rapid line corrosion, cuprous chloride and copper sulphate would be formed. There would probably be a tendency for the reaction products to move downward, under the action of gravity, toward the solution-air interface. The cuprous chloride, being insoluble, would be deposited over the flashing and oxidized, in part at least, to basic cuprous chloride by oxygen diffusing through to the deposit. This deposit would form an effective barrier to the further passage of oxygen, thus reinforcing the action of the roofing in preventing access of the air to the underlying copper. Any movement of copper sulphate downward would result in a greater concentration near the edge of the roofing. This may be a factor in the localization of the corrosion.

If line corrosion is to take place on copper-valley flashings, three conditions must be fulfilled. First, the rain water falling on the roof must be contaminated by the atmosphere and by dust and dirt from the roof. The results of the first series of tests, and the fact that the known failures of flashings have occurred in cities not far from

the seacoast, suggest that line corrosion will not be serious except in the presence of both sulphur dioxide and sodium chloride. Second, rain water must be retained in contact with the flashing for an appreciable time after rainfall has ceased in such a manner that part of it is exposed freely to the air and part of it is shielded. And third, if the line corrosion is to occur in copper, the retained water must not be stirred or agitated. (Compare the results on specimen No. 15 of the second series of tests.) The remedy for line corrosion will consist of preventing the accumulation of any solution in such a manner that differential aeration may occur. The Type IV construction fulfills the necessary conditions in so far as is possible with a reasonably simple and inexpensive construction.

V. SUMMARY

The following conclusions are based on the results of the tests supplemented by data obtained from studies of flashing failures:

1. Line corrosion of valley flashings can be reproduced by accelerated corrosion tests.
2. Wood shingles are not the primary cause of line corrosion.
3. Line corrosion may occur not only with wood shingles but also with slate, asbestos shingles, composition shingles, and, under exceptional circumstances, even when one sheet of copper overlaps another.
4. A solution containing a mixture of sulphur dioxide and sodium chloride produces line corrosion far more rapidly than solutions of either substance alone.
5. The rate at which line corrosion proceeds depends on the solution and on the time during which the solution remains without motion in contact with the flashing.
6. The length of time for which the solution remains in contact with the flashing after a rainfall depends on the porosity of the roofing. Hence, the more porous and absorbent the roofing material, the more rapid will be the corrosion.
7. On all open-valley flashings, particularly in cities near the seacoast where line corrosion may be expected, a batten strip should be inserted between the flashing and the roofing. This batten strip should be a smoothly finished hardwood strip, preferably waterproofed, having the approximate dimensions of a lath. It should be placed about 1 inch back of the edge of the roofing and nailed firmly and tightly to the flashing. There is reason to believe that, if this precaution is followed, no perceptible line corrosion will occur in 50 years or more of service on a roof under the severe conditions such as are found in New York City and its environs.

WASHINGTON, July 10, 1929.

COMPARATIVE PROPERTIES OF WROUGHT IRON MADE BY HAND PUDDLING AND BY THE ASTON PROCESS

By Henry S. Rawdon and O. A. Knight

ABSTRACT

The hand-puddling method of making wrought iron has not greatly changed for a century. More economical methods in the manufacture of this product is the crying need of the industry. A radically new process, recently developed, is now coming into commercial use, in which pig iron, which has been refined in a Bessemer converter, is poured into molten slag so as to produce intimate mingling of the two. A comparison of the properties of wrought iron made thus with that made by hand puddling forms the subject of this report. The test results failed to show any marked difference in the products of the two processes. The new product appears to have all of the essential properties usually connoted by the name—wrought iron.

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I. INTRODUCTION

The need for more economical methods in the manufacture of wrought iron has long been recognized. As stated by Aston,[1] the outstanding needs of the wrought-iron industry are: Decreased cost of production and increased tonnage, the former being the more essential of the two. The realization of the importance of these needs is by no means new in the history of the industry. Shortly after the advent of the Bessemer process for manufacturing steel, attempts were started [2] for increasing the scale of production of wrought iron and these attempts have continued down to the present day, some of the processes developed being used commercially with very considerable success. Practically all of the processes, with one notable exception, which have attained any degree of prominence or success attempted to duplicate in a mechanical way the operations of hand puddling, this being generally done by means of a movable furnace. The characteristic features of the present-day mechanical-puddling processes for the manufacture of wrought iron have been described in the technical literature,[3] and further reference to them here is unnecessary. A few years ago a series of comparative tests was made by the Bureau of Standards of wrought iron made by one of these processes (footnote 3 (*c*)), together with wrought iron made by the same company by the usual hand-puddling method from pig iron of the same heat. One of the conclusions expressed as a result of these tests, a report of which has been published,[4] was as follows:

> The tests of two lots of wrought iron made by two distinctly different puddling processes have not shown anything to indicate that the hand-puddling product can not be equaled in an iron made by a mechanical-puddling process.

About a year ago the attention of this bureau was directed to the successful development, on a commercial scale, of a process for the production, by a very novel process, of a wrought iron which appears to possess the essential characteristics which are usually associated

[1] James Aston, Trend of Development in the Wrought Iron Industry, Am. Inst. Min. Met. Eng., Pamphlet No. 1595–C; October, 1926.

[2] Thomas Turner, Metallurgy of Iron, 5th ed., p. 387, Charles Griffin & Co.; 1918.

[3] Symposium on Wrought Iron: (*a*) H. E. Smith, Manufacture and Use of Wrought Iron; (*b*) F. H. Dechant, Ely Process of Mechanical Puddling for the Production of Wrought Iron; (*c*) J. P. Roe, Roe Puddling Machine; (*d*) James Aston, Problem of Wrought Iron Manufacture and a New Process for Its Production, Am. Iron & Steel Inst. Yearbook, **15**, p. 117; 1925. See also footnote 1.

[4] Henry S. Rawdon and Samuel Epstein, Observations on Phosphorus in Wrought Iron Made by Different Puddling Processes, Amer. Iron & Steel Inst. Yearbook, **16**, p. 117; 1926.

with the time-honored product of the hand-puddling method. This new process differs radically in a good many respects from the conventional method of puddling. In this process, which will be referred to hereinafter as the "Aston process," after its inventor, Dr. James Aston, the essential objects accomplished in the puddling process as ordinarily understood, are attained in a unique manner. The melting of the raw material (pig iron) is done in a cupola, the refining of the molten metal in a Bessemer converter, the production of the slag of proper composition in an open-hearth furnace by itself, and the mechanical disintegration of the iron and the incorporation of the slag with it are attained by pouring a charge of the molten refined iron into a bath of the molten slag. The squeezing of the "ball" of iron into convenient form for working, although done somewhat differently from the method ordinarily employed with the hand-puddled product, involves no new principle, nor does the mechanical working of the squeezed iron into suitable form for handling in the subsequent operations.

This process has definitely passed the experimental stage and the product is now being produced on a tonnage basis, practically all of it being used in the manufacture of pipe. The United States Government is a purchaser of considerable amounts of wrought-iron pipe and has drawn up specifications [5] covering such material. In view of this fact, therefore, together with the interest of the Bureau of Standards in obtaining information on new important industrial processes, a study of the properties of this material by the bureau was deemed both proper and desirable when the bureau was approached by the manufacturers in this matter. The study was undertaken on the research associate plan,[6] the investigator appointed for carrying out the work being O. A. Knight, associate professor of metallurgy, the Pennsylvania State College. The work was supported by the manufacturers, the A. M. Byers Co.

1. RÉSUMÉ OF THE ASTON PROCESS

This process differs from puddling, as ordinarily understood, in that the various objects to be accomplished are brought about as distinct steps carried out in separate furnaces or other units, instead of being a single-furnace process the nature of which gradually changes as it proceeds. The description of the operations given below is based upon observations made in the mill and represents the practice at the time the observations were made, but not necessarily all details as carried out at present. In melting the pig iron, which was of Bessemer grade, standard cupola melting practice was

[5] Federal Specifications Board specification No. 242, Pipe, Wrought Iron; 1925.
[6] B. S. Circular No. 206, Research Associates at the Bureau of Standards.

followed. Mention should be made of the treatment of the molten metal with soda ash to offset sulphur "pick-up" in the cupola. About 40 to 50 pounds of soda ash (anhydrous sodium carbonate) was placed in the ladle into which a charge of approximately 5,500 pounds of molten metal was tapped from the cupola. A period of about 15 minutes was required for this amount of metal to flow and this insured thorough mixing and plenty of time for the desulphurizing reactions to occur. The metal in the ladle was then skimmed free from slag and charged into the Bessemer converter.

A 2-ton side-blown converter was used, the "blow" usually lasting about 18 minutes. The composition of the blown metal is given in Table 1. After blowing, the metal was tapped into a lip-pour ladle and the slag raked off. No additions of manganese, silicon, aluminum, or other deoxidizing or degasifying agents, such as are used in steel manufacture, were employed. The metal was "shotted" in the condition as teemed from the converter. The ladle of metal was conveyed by means of a crane, which also carried scales for weighing the charge, to the "shotting cup" for the "shotting" operation, that is, the treatment of the metal with slag. Working drawings of one of the cups, which were made of cast iron and lined with fire brick, are given in Figure 1. A number of these cups, to be used in succession, are necessary in regular mill procedure.

TABLE 1.—*Results of chemical analysis of metal at different stages of process*[1]

Cupola iron [2]					"Blown" metal [2]					Wrought-iron muck, bar [2]					
Before soda-ash addition	After soda-ash addition														
S	Mn	S	P	Si	C	Mn	S	P	Si	C	Mn	S	P	Si	Slag and oxides[3]
0.072	0.56	0.039	0.098	1.44	0.08	0.02	0.048	0.100	0.026	0.02	0.03	0.031	0.100	0.122	2.46
.057	.49	.039	.103	1.02	.07	.04	.040	.103	.028	.03	.04	.027	.097	.132	4.17
.083	------	.044	------	1.09	.06	------	.057	------	.015	.03	.03	.037	.118	.103	2.98
.127	------	.044	------	1.14	.06	------	------	------	.010	.02	.03	.042	.112	.132	3.53
.098	------	.048	------	1.13	.07	------	.051	------	.014	.03	.05	.042	.130	.190	4.25
.088	------	.056	------	1.19	.06	------	.060	------	.011	.03	.04	.043	.126	.202	4.30
.111	------	.050	------	1.18	.06	------	.060	------	.017	.03	.04	.038	.120	.132	3.12
.084	------	.040	------	.99	.07	------	.046	------	.010	.03	.04	.037	.120	.121	3.08
.079	------	.040	------	.93	.08	------	.048	------	.008	.03	.04	.031	.124	.130	4.00
.079	------	.035	------	1.18	.08	------	.043	------	.010	.02	.04	.028	.124	.174	4.84
.091	.51	.043	.096	1.15	.06	.03	.056	.104	.014	.02	.03	.042	.120	.146	4.07
.100	------	.042	------	1.02	.06	------	.045	------	.015	.02	.03	.038	.148	.125	3.32
.110	------	.044	------	1.23	.08	------	.058	------	.012	.03	.04	.040	.126	.144	3.86

[1] The data given here were taken at random from the daily laboratory records of the A. M. Byers Co., covering a period of about 6 months at the mill at Warren, Ohio, by O. A. Knight.
[2] All figures are in percentages.
[3] Method described by Westcott, Eckert, and Einert, Ind. Eng. Chem., **19**, p. 1285; 1927.

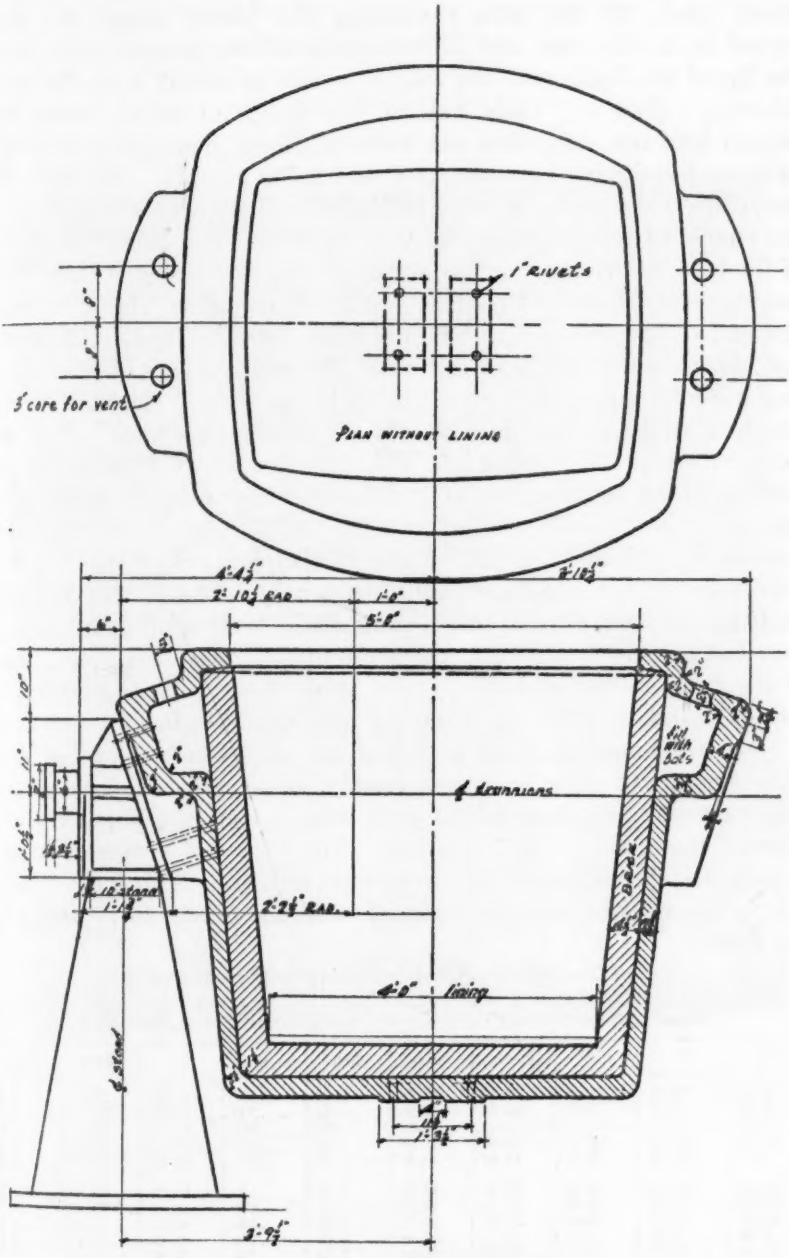

FIGURE 1.—*Drawing of the shotting cup*

Furnished by the manufacturers.

The shotting operation was carried out as follows: (1) Molten slag was poured into one of the cups until it was slightly less than two-thirds filled, (2) the ladle containing the blown metal was then moved up to this cup, and (3) molten metal was poured slowly over the lip of the ladle into the slag at a rate of about 1 ton in three minutes. (Fig. 2.) Only half of the charge of blown metal was poured into one cup, thus one ladle of blown metal furnished two balls, each weighing between 2,200 and 2,500 pounds. By observing the scale on the crane carrying the ladle a rather accurate division of the charge of the molten metal was possible. The height of the lip of the ladle above the slag surface in the cup was about 9 feet. The practice was followed of pouring about 800 pounds of the metal near one end of the cup, a like amount near the other end, and the remainder near the middle of the cup. The temperature of the molten slag must be maintained considerably below that of the molten iron which is to be poured into it. If no precautions were taken the temperature of the slag might rise sufficiently, as a result of the heat liberated by the iron as it passes from the liquid state upon quenching, to interfere seriously with the efficacy of the slag as a quenching medium. An undue rise of temperature of the slag was prevented by throwing a shovelful of cold granulated slag into the shotting cup from time to time. This also served to prevent "boiling over" of the slag in the cup, which might otherwise occur as a result of the vigorous gas evolution which takes place when the stream of molten metal is poured into the molten slag. During the course of the shotting operation the cup had the appearance of being full. However, the boiling subsided quickly as soon as the last of the molten metal had been added and, when quiet, the cup was only slightly more than two-thirds full. The excess slag was then decanted into the cup which was to be used next (fig. 3), and the "ball" was dumped onto a carriage (fig. 4) and was ready to be taken to the press.

TABLE 2.—*Results of chemical analysis of shotting slag* [1]

Before shotting [2]				After shotting [2]					
SiO_2	Fe	FeO	Fe_2O_3	SiO_2	Mn	P	Fe	FeO	Fe_2O_3
8.04	66.46	78.93	7.36	7.78	0.96	0.197	66.36	77.98	8.38
8.56	65.15	71.69	13.44	8.90	.92	.200	64.94	74.55	9.97
7.80				9.32	.90	.235	65.07	72.03	12.96
10.92	65.66	71.31	14.60	11.08	.92	.352	64.07	75.68	7.46
8.56	65.06	70.49	14.64	10.58	.88	.336	62.85	71.78	10.05
10.28	66.84	70.32	17.37	12.88	1.16	.440	63.21	73.10	9.11
10.00	64.09	70.32	13.46	10.54	.96	.384	63.90	73.73	9.38
10.26	62.51	70.00	11.55	10.36	1.05	.420	62.12	72.79	7.89
9.30	63.93	65.93	17.96	10.42	1.03	.364	63.20	70.13	12.40
10.12	64.60	69.31	15.30	10.34	1.13	.424	63.90	72.40	10.87
9.00	65.40	65.84	20.31	10.48	1.10	.440	64.10	69.83	14.01
9.74				9.98					
10.16	66.80	72.92	14.44	10.86	1.03	.380	65.30	74.43	10.73
10.10	65.96	63.69	23.38	11.78	1.07	.392	63.69	69.26	14.04

[1] The data given here were obtained in the same manner as those in Table 1.
[2] All results are in percentages.

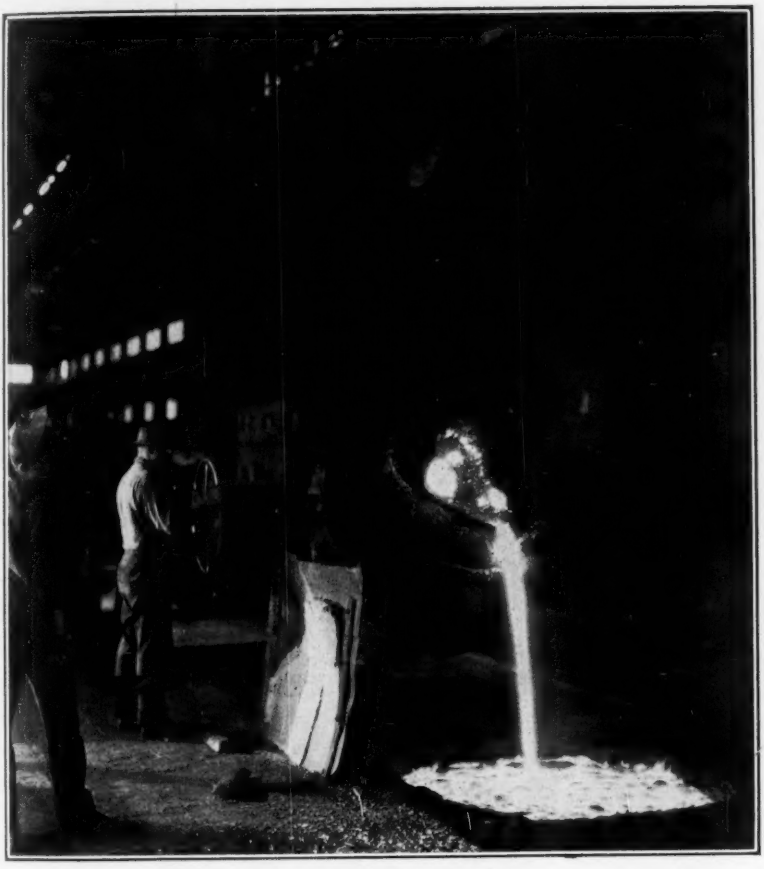

FIGURE 2.—*The shotting operation*

The metal in the tilted ladle has just come from the Bessemer converter where it has been "blown." Note the surface of the slag in the lower container, the shotting cup, which nearly reaches the top of the cup on account of the vigorous gas evolution produced by pouring the molten metal into the molten slag.

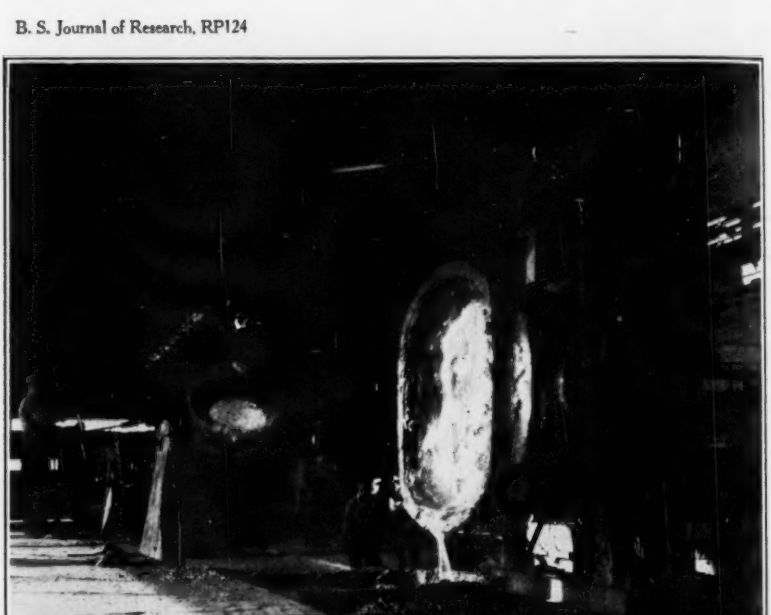

FIGURE 3.—*Decanting the excess slag after the shotting operation*

The slag is poured into another cup to be used for shotting the next ladle of metal. Note the ball within the upper cup.

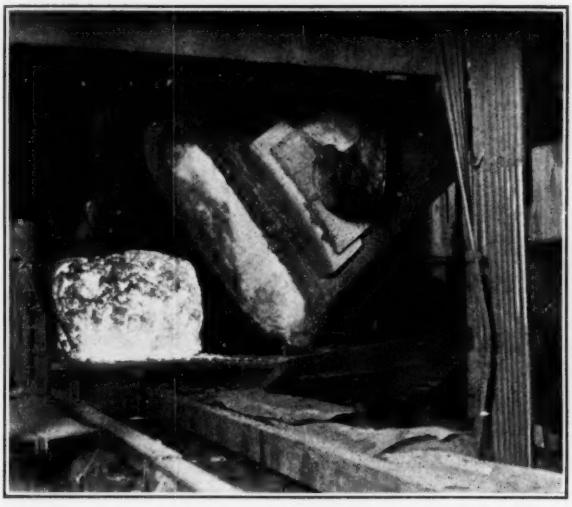

FIGURE 4.—*The ball after being dumped from the shotting cup*

It is now ready for the squeezing operation.

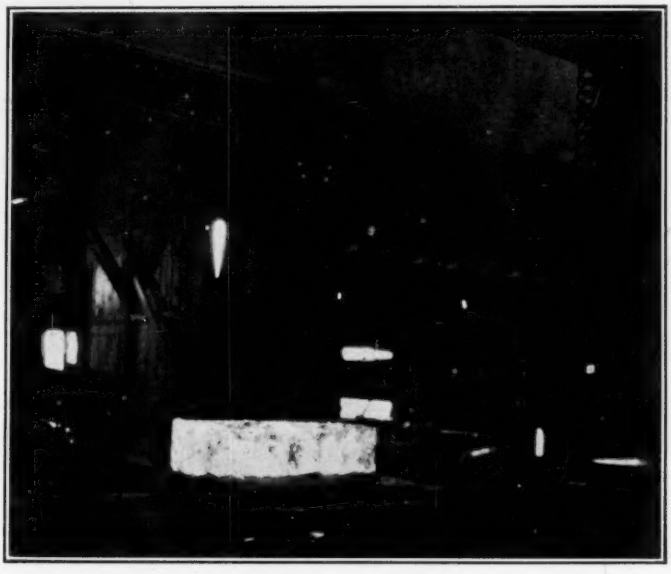

FIGURE 5.—*The bloom as it comes from the press*

Much of the slag has been squeezed out and the material is quite compact. It is now ready for the rolling mill where it will be rolled into muck bar.

The slag into which the metal was poured in the shotting operation was prepared in a 15-ton tilting open-hearth furnace. The composition of this slag was close to the average composition of that which is formed in ordinary puddling. (Table 2.) The effect produced by the shotting operation evidently depends mainly upon the difference in temperature between metal and slag and the evolution of gas which occurs when the two materials are brought together. Previous observations in the mill had indicated that the temperature of the molten slag within the cup was somewhat above 1,315° C. (2,400° F.), whereas the temperature of the molten metal was considerably higher, being approximately 1,540° to 1,590° C. (2,800° to 2,900° F.). The sudden violent evolution of gas which occurs as the metal is poured into the slag comminutes it into a relatively fine state of division, thus facilitating the incorporation of the slag within the metal. The particles of metal accumulate in the lower part of the cup and agglomerate into a coherent spongy mass or "ball" resembling in all essential respects, except size, that taken from the puddling furnaces.

The squeezing of the ball to free it from excess slag did not differ in principle from the similar operation in connection with ordinary puddling. In this case, however, a hydraulic press which squeezed the ball on the four sides and the ends was used. A fairly compact bloom measuring approximately 12 by 14 inches by 5 feet was the result. The bloom is shown in Figure 5 on its way to the rolling mill, where it was given nine passes in a 29-inch mill and seven in a 24-inch mill which reduced it to the form of muck bar three-fourths inch thick by 8 inches wide. The composition of the muck bar is given in Table 1. The lower carbon content of the muck bar as compared to the blown metal is to be attributed to the effect of the shotting. The increase in the silicon content is, of course, the result of the mechanically included slag. The effect of the desulphurizing action of the soda-ash treatment of the cupola metal is unmistakable. It would appear also that a slight decrease in sulphur content accompanies the shotting operation.

II. PURPOSE AND SCOPE OF THE INVESTIGATION

As stated above, iron made by the Aston process is now a commercial product, being sold under the same designation as is the product of the older and more familiar puddling process, and intended for the same usage. It has been tacitly assumed by the manufacturers that the two materials are not essentially different and that the newer product, regardless of the novel features of its method of production, is fully entitled to the name, "wrought iron."

The matter of the definition of wrought iron; that is, whether this material should be defined mainly in terms of the process by

which it has been produced or by the properties which it possesses is of some importance in the preparation of specifications. It was considered, however, that a determination of the properties of the new wrought iron, particularly as compared with those of wrought iron made by the hand-puddling process, was a matter for more immediate consideration. This was made the main purpose of the investigation, therefore, and this report summarizes the results obtained in a comparison of the properties of the two types of material. Both materials are referred to herein as "wrought iron" for convenience in discussion. It is believed that the question of the inclusion of the new product under the term "wrought iron" in specifications is a matter that will automatically settle itself one way or the other in accordance with the degree of similarity of the two types of materials.

III. MATERIALS AND METHODS

1. MATERIALS

(a) PIPE

Since iron made by the Aston process is being used commercially only in the form of pipe, the majority of the tests which were carried out were on pipe materials. In addition to the tests of the finished pipe, 1-inch butt-welded pipe being used throughout, similar tests were made on the pipe skelp, and on the muck bar, or "first rolling," which is the product which is sheared into short lengths, piled together, reheated, and rolled into the form of skelp. Some observations were also made upon the ball before it had been subjected to any working whatsoever. In all cases the tests were carried out on both hand-puddled iron and on the new product, the two materials being the products of the same manufacturer. In the case of skelp and pipe, similar tests were also made on a composite iron made by using 50 per cent of each of the two irons in the form of sheared muck bar in forming the "pile" which was heated and rolled into the form of skelp. The pile was similar to a sandwich in that the hand-puddled iron formed the surface layers and the new-process iron the central part. All samples used throughout were taken under the supervision of the authors and represent "run-of-mill" material, unless stated otherwise.

In selecting the samples of muck bar and skelp, four different strips were chosen at random, as they were rolled, and pieces were cut from three positions along the length representative of the "front," "middle," and "back" of the strip as rolled. The purpose

of using three samples from a single strip was to show the degree of uniformity of the material. The pipe samples were 10-foot lengths of commercial black pipe of the three kinds—hand-puddled iron, new-process, and the composite iron formed of equal parts of the other two. Three samples of each kind of pipe were used, the selection in each case being made at random.

The identification mark, which was stamped on each sample at the mill, was chosen so as to show (*a*) the nature of the iron (HP, hand-puddled iron; A, iron made by the Aston process; AHP, the composite iron); (*b*) the position of the sample in the strip, skelp, or muck bar, as rolled (F, front; M, middle, B, back); and (*c*) the number of the sample strip or pipe (1, 2, 3, 4). Thus, for example, "HPF1," as relating to skelp indicates the piece cut from the front end of the hand-puddled skelp strip No. 1. These designations will be used in summarizing the test results later in this report.

(b) ROUNDS

In addition to the tests on pipe materials, some work was done on 1-inch rounds of the new wrought iron. Although the new product is not being used commercially in this form, as yet, wrought iron in this form is widely used. These rounds were prepared especially for this work. By using material in this form it was possible to carry out a number of additional tests which were not practicable with the pipe materials. A rather extensive series of tests on 1-inch rounds of high-grade hand-puddled wrought iron made by several different manufacturers has already been carried out by the bureau,[7] and the results of these tests were used for comparison with those obtained with the new iron.

Three lots of 1-inch rounds were rolled from the same bloom, 11½ by 13 inches in cross section, the amount of working received being different for the three. In the preparation of one lot, which will be referred to as "direct rolled," the bloom was rolled, without reheating, into a billet, 4 by 4½ inches in section, a part of which, after reheating, was rolled directly into the form of 1-inch rounds. In the preparation of the other two lots the rolling of the billet was carried far enough to produce muck bar, ¾ by 4½ inches in section, which was then sheared into shorter lengths, assembled into 8-high piles and reheated. One pile was rolled directly into 1-inch rounds, which will be referred to as "single refined." Another 8-high muck-bar pile, after reheating, was rolled into bar form, ⅜ by 4½ inches in section. This, in turn, was sheared into short lengths, assembled

[7] H. S. Rawdon and S. Epstein, The Nick-Bend Test for Wrought Iron, B. S. Tech. Paper No. 252; 1924. Proc. Am. Soc. Test. Mtls., 22, Pt. II, p. 193; 1922.

into an 8-high pile, reheated, and rolled into 1-inch rounds. This lot of material will be referred to as "double refined."

(c) SLAG

The observations which were made upon the slag were on rather large masses of the slag as well as upon slag recovered from the finished pipe. In the case of the Aston process, a small "ingot" of slag was poured into a chill mold, whereas in the puddling process a rather large piece was raked out of the furnace. Observations were also made on samples obtained by collecting the slag as it dripped from the ball.

2. METHODS

In addition to the test methods which are commonly found in specifications for wrought-iron pipe and bar stock, a number of other tests were used, which, it was thought, might reveal important differences in the materials if they existed. Chemical analyses were made of both iron and slag. The physical testing methods used included density determinations as well as the usual tension, torsion, impact, and flattening tests. The structural examination of the materials, from both the microscopic and the macroscopic aspect, constituted an important part of the study. Laboratory corrosion tests were carried out on the finished pipe by various accelerated methods in both tap water and sea-salt solution, together with some observations on the relative electrolytic solution potentials of the two types of iron. Observations were also made in the mill for the purpose of comparing the behavior of the irons in welding, galvanizing, and machining.

IV. RESULTS

1. COMPOSITION

The samples used for chemical analysis consisted of short lengths from each end of three 10-foot lengths of the new-process iron pipe, from each end of a similar length of hand-puddled iron pipe, and from each end of a similar length of pipe made of the composite iron. The results are given in Table 3. It is apparent from these results that there is no marked difference in composition between iron made by hand puddling and that made by the new process. The carbon and phosphorus contents were found to be consistently lower in the new iron than in the hand-puddled product, but the sulphur content was somewhat higher. The latter was lower than the average shown by the mill analyses made on muck bar (Table 1), as was the carbon content also.

TABLE 3.—*Results of chemical analysis of the three types of pipe used* [1]

[A=new-process iron, HP=hand-puddled, AHP=composite iron; x and y indicate the two ends of the pipe; 1, 2, or 3 indicate the number of the pipe]

Pipe material	Determination							
	C	Mn	P (total)	S	Si	Slag [2]	P (slag)	Cu
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A1x	0.02	0.03	0.100	0.031	0.11	2.6	0.055	0.02
			.100			2.7		
A2x	.01	.03	.105	.031	.12		.060	
A2y			.100					
A3x	.01	.03	.100	.034	.12	2.5	.055	
A3y			.100					
HP1x	.03	.04	.150	.019	.22	3.0	.075	
HP1y			.145					
AHP2x	.01	.03	.135	.022	.16	3.0	.070	
AHP2y			.135					

[1] Analysis by H. A. Bright, associate chemist, Bureau of Standards.
[2] Iodine method. *See* Proc. Am. Soc. Test. Materials, **25**, pt. 1, p. 79; 1925.

The chemical composition of the slag used in the Aston process and that produced in the hand-puddling process was determined. In each case a large lump of slag, as stated above, was used for sampling, as well as slag drippings from the wrought-iron ball. In addition, analyses were made of the slag recovered by dissolving a sample of the pipe in an iodine-potassium-iodide solution. The results are given in Table 4.

TABLE 4.—*Chemical composition of slag* [1]

Material	Determination						
	FeO	Fe_2O_3	SiO_2	P_2O_5	MnO	CaO	Al_2O_3
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Slag, Aston process, lump	71.0	10.3	12.0	1.2			
Same, recovered from the pipe [2]	57.0	25.0	9.0	2.0	1.4	0.4	1.2
Same, obtained as "drippings from the ball"	70.7	8.9	11.6	1.34	1.76		2.0
Slag, hand-puddling process, lump	66.2	7.2	14.8	3.1			
Same, recovered from the pipe [2]	63.0	12.0	14.0	3.0	1.8	<1.0	5.0
Same, obtained as "drippings from the ball"	67.5	14.5	11.5	1.56	1.55		2.4

[1] Analysis by H. A. Bright and C. P. Larrabee, Bureau of Standards.
[2] The slag was separated from the pipe by the iodine method.

The composition of the slag used in the new process, as determined on a lump sample, agreed well with the average composition shown by the mill laboratory records. The differences in composition of the two types of slags (as determined on comparable samples) were slight. Too much significance should not be attached to the apparent difference in composition of the slags determined on the residues obtained by dissolving a sample of the finished pipe as compared with the same slags in lump form. The $Fe_2O : FeO_3$ ratio of slag recovered as a residue after dissolving the iron may be altered as a result of the method used in recovering the slag.

2. DENSITY

The density of the three irons in various stages of working was determined, the results being summarized in Table 5. On account of the porosity of these materials, the results should not be considered as indicating in all cases the true density. The results agree well, however, with other published results for the density of wrought iron and are believed to give reliable indications as to the relative densities of the three materials and of the variations in density in any one product. It will be noted that the average density of the iron made by the Aston process was consistently slightly higher in all of the products than that of the other two irons. In the case of the pipe, however, the difference between maximum and minimum for the new-process material was slightly greater than for the other pipe.

TABLE 5.—*Density of wrought iron in various stages of working* [1]

[A=iron made by Aston process; HP=hand-puddled iron; AHP=composite iron containing 50 per cent of each A and HP. F, M, and B=front, middle, and back, respectively, x and y indicate the two ends of the pipe length]

Material			Density, g/cm³, 25° C.
Process	Rolled product	Sample	
Aston	Muck bar	AF1	7.63
		AM1	7.65
		AB1	7.58
		AF4	7.61
		AM4	7.57
		AB4	7.65
Average			7.615
Hand-puddled	Muck bar	HPF1	7.53
		HPM1	7.55
		HPB1	7.60
		HPF2	7.61
		HPM2	7.62
		HPB2	7.64
Average			7.59
Aston	Skelp	AF3	7.67
		AM3	7.66
		AB3	7.66
		AF4	7.68
		AM4	7.67
		AB4	7.68
Average			7.67
Hand-puddled	Skelp	HPF1	7.64
		HPM1	7.65
		HPB1	7.67
		HPF4	7.64
		HPM4	7.63
		HPB4	7.66
Average			7.65

[1] Density measurements by E. L. Peffer, physicist, Bureau of Standards.

TABLE 5.—*Density of wrought iron in various stages of working*—Continued

Material			Density, g/cm³, 25° C.
Process	Rolled product	Sample	
Composite	Skelp	AHPF1	7.61
		AHPM1	7.64
		AHPB1	7.64
		AHPF4	7.64
		AHPM4	7.63
		AHPB4	7.64
Average			7.63
Aston	Pipe	A1x	7.68
		A1y	7.66
		A2x	7.66
		A2y	7.65
		A3x	7.61
		A3y	7.64
Average			7.65
Hand-puddled	Pipe	HP1x	7.62
		HP1y	7.62
		HP2x	7.63
		HP2y	7.61
		HP3x	7.61
		HP3y	7.62
Average			7.62
Composite	Pipe	AHP1x	7.61
		AHP1y	7.62
		AHP2x	7.61
		AHP2y	7.61
		AHP4x	7.62
		AHP4y	7.63
Average			7.62

3. MECHANICAL PROPERTIES

(a) PIPE MATERIALS

The behavior of the three irons, in the form of muck bar, skelp, and pipe was determined under tension. Torsion tests and also flattening tests were made of the finished pipe.

(1) TENSILE PROPERTIES.—The tensile properties of the iron in the form of muck bar (one-half inch thick) were determined on 20-inch specimens with a reduced section 1½ inches wide. The elongation was measured over both an 8-inch and a 2-inch length. The skelp specimens were of the same size, except in thickness which was that of the skelp strip as rolled. This was approximately 0.133 inch, including the surface scale (0.03 inch), which flaked off during the test. All of the tests were made with an Amsler tension testing machine of 50,000 pounds capacity. For a number of the specimens of each of the three irons, the Ewing extensometer was used in order to obtain the necessary data for the stress-strain curves. These curves for the muck bar and skelp are given in Figures 6 and 7, respectively.

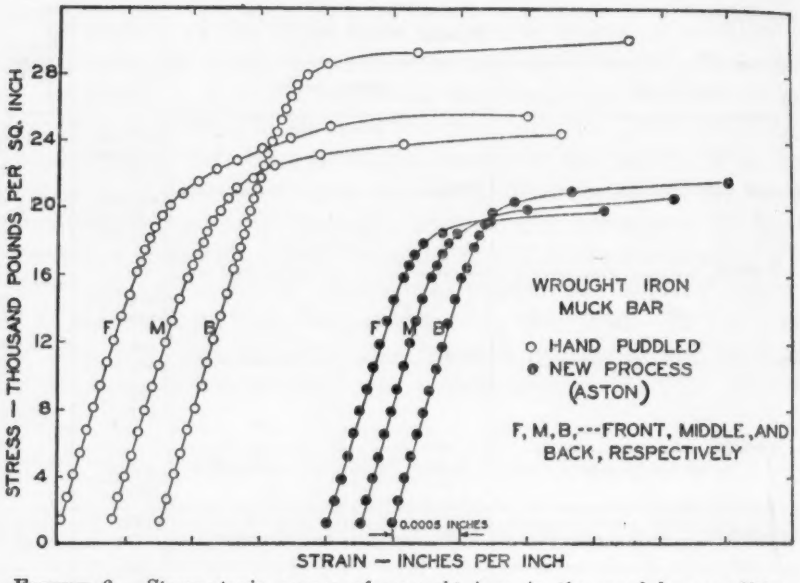

FIGURE 6.—*Stress-strain curves of wrought iron in the muck-bar condition tested in tension*

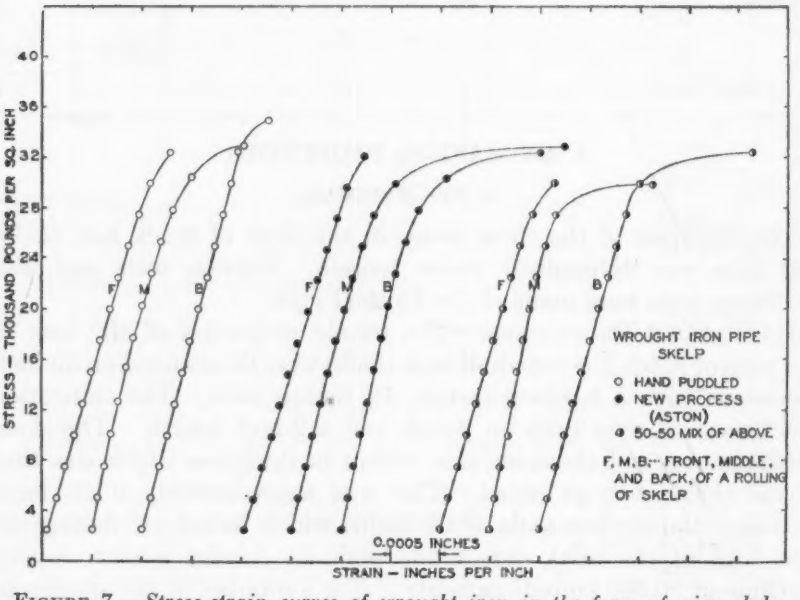

FIGURE 7.—*Stress-strain curves of wrought iron in the form of pipe skelp tested in tension*

The tensile properties of the two irons in the muck-bar state are summarized in Table 6 and of the skelp in Table 7. Here and elsewhere, the test results have been "rounded off" to the nearest 50 pounds.

Tension tests of the pipe were made on full-size specimens as well as on strips machined from the pipe. The average dimensions of the pipe, which was nominally a 1-inch pipe, were: Inner diameter, 1.05 inches; outer diameter, 1.325 inches. Eighteen-inch specimens from each end of three lengths of pipe were used. Snugly fitting plugs of mild steel were inserted in the ends of the pipe specimens to prevent them from collapsing in the jaws of the testing machine. The length of specimen between the jaws was about 10 inches. The results of these tests are given in Table 8.

TABLE 6.—*Tensile properties of wrought iron in the muck-bar state*

[A=iron made by Aston process; HP=hand-puddled iron; F, M, and B=front, middle, and back of the muck-bar strip as rolled]

Material	Tensile properties				
	Yield point [1]	Ultimate tensile strength	Elongation		Reduction of area
			2-inch	8-inch	
	Lbs./in.²	*Lbs./in.²*	*Per cent*	*Per cent*	*Per cent*
AF4	21,300	32,800	12.5	6.5	12.5
AF4	20,800	43,300	34.0	21.5	20.0
AF4	20,000	38,500	18.5	11.5	15.5
AM4	20,850	38,000	17.5	10.5	11.0
AM4	20,650	41,350	28.5	18.5	19.5
AM4	20,000	31,450	[3]	[3]	7.0
AB4	21,800	39,900	25.0	12.5	18.0
AB4	21,200	42,250	27.5	20.0	19.5
AB4	21,250	43,500	27.5	22.5	26.5
Average	20,870	39,000	23.9	15.4	16.4
HPF1	[2]	[3] 13,600			
HPF1	25,500	40,350	17.5	9.5	10.5
HPM1	24,300	34,000	[4]	5.5	5.5
HPM1	27,000	40,550	12.5	6.5	9.0
HPB1	29,400	42,400	13.5	7.0	10.0
HPB1	28,000	49,300	18.5	13.8	18.0
Average	26,840	41,320	15.5	8.4	10.6

[1] From stress graph drawn by the Amsler machine.
[2] Broke outside of gage marks.
[3] Broke within the jaws of the machine at a weak spot.
[4] Specimen too rough to show the gage marks.

TABLE 7.—*Tensile properties of wrought iron in the form of pipe skelp*

[A=iron made by Aston process; HP=hand-puddled iron; AHP=composite iron, equal parts of A and HP; F, M, and B=front, middle, and back of the strip of skelp as rolled]

Material	Tensile properties				
	Yield point [1]	Ultimate tensile strength	Elongation		Reduction of area
			2-inch	8-inch	
	Lbs./in.[2]	*Lbs./in.*[2]	*Per cent*	*Per cent*	*Per cent*
AF1	29,550	44,100	26.5	21.0	24.1
AF1	33,100	47,200	30.0	22.5	23.7
AM1	30,550	44,950	22.3	18.0	20.2
AM1	31,000	48,000	27.5	17.5	22.3
AB1	31,800	47,200	33.0	24.5	25.2
AB1	30,550	45,800	28.0	22.5	21.6
AF2	32,000	44,600	21.0	17.0	21.6
AF2	28,800	44,400	20.0	15.0	16.6
AM2	27,100	41,600	17.5	12.0	17.2
AM2	29,700	44,550	[3]	[3]	[3]
AB2	30,450	42,400	16.0	11.5	15.2
AB2	32,500	45,000	20.0	16.0	19.0
AF3	29,850	44,500	19.0	16.5	16.4
AF3	28,750	43,000	16.0	12.0	17.0
AM3	28,600	44,200	20.0	14.0	16.7
AM3	26,500	42,000	15.0	12.3	15.0
AB3	31,900	45,000	20.0	11.5	19.5
AB3	30,450	42,150	19.0	13.2	17.7
AF4	29,500	44,650	32.5	20.5	24.0
AF4	32,650	46,900	20.0	12.5	17.8
AM4	31,500	48,200	17.5	15.0	22.0
AM4	28,300	44,550	21.0	16.0	18.5
AB4	32,000	45,500	25.0	21.0	23.5
AB4	32,500	48,200	22.5	14.5	20.3
Average	30,400	44,940	22.8	16.3	19.7
HPF1	32,500	46,000	16.0	11.0	18.0
HPF1	34,000	45,150	13.0	9.5	13.7
HPM1	31,300	46,700	19.0	13.0	16.6
HPM1	32,000	47,250	17.0	13.5	17.0
HPB1	33,600	47,250	17.5	12.5	16.0
HPB1	36,100	46,750	17.0	12.0	17.6
HPF2	32,350	46,550	20.0	15.0	18.1
HPF2	34,000	44,350	12.0	9.0	14.7
HPM2	31,500	40,500	10.0	6.2	11.5
HPM2	32,350	42,800	[3]	[3]	9.9
HPB2	36,500	46,250	15.0	10.0	12.0
HPB2	36,450	47,800	17.5	14.5	15.2
HPF3	33,000	42,000	11.5	7.5	11.5
HPF3	34,350	45,950	18.0	13.0	17.1
HPM3	32,050	42,400	[3]	[3]	
HPM3	32,000	45,550	13.5	10.2	15.5
HPB3	33,850	43,450	12.5	9.0	9.5
HPB3	34,000	43,000	14.0	8.0	14.5
HPF4	34,500	43,500	11.0	5.5	10.5
HPF4	34,150	42,300	11.0	8.0	15.5
HPM4	34,850	45,450	10.0	6.0	9.1
HPM4	33,000	41,100	7.5	4.5	7.1
HPB4	33,850	45,000	12.5	9.5	13.5
HPB4	36,300	46,450	12.0	6.2	8.1
Average	33,690	44,730	14.0	9.8	13.5
AHPF1	32,150	41,100	8.5	6.0	10.5
AHPF1	31,750	42,500	12.0	8.0	13.0
AHPM1	31,500	40,500	[3]	[3]	13.0
AHPM1	31,950	43,100	12.5	9.0	12.5
AHPB1	32,850	42,800	12.5	9.0	11.5
AHPH1	31,750	40,000	10.5	6.5	9.5
AHPF2	31,000	38,000	9.0	5.5	10.0
AHPF2 [4]	30,300	31,300	6.5	2.0	9.5
AHPM2	30,050	39,400	11.0	7.0	13.3
AHPM2	28,850	36,050	9.0	4.5	11.5
AHPB2	34,150	43,550	18.5	14.0	16.3
AHPB2	31,250	40,750	12.0	7.5	13.5

[1] From stress graph drawn by Amsler machine.
[2] Broke in fillet.
[3] Broke outside of gage points.
[4] Rough defective specimen.

TABLE 7.—*Tensile properties of wrought iron in the form of pipe skelp*—Continued

[A=iron made by Aston process; HP=hand-puddled iron; AHP=composite iron, equal parts of A and HP; F, M, and B=front, middle, and back of the strip of skelp as rolled]

Material	Tensile properties				
	Yield point	Ultimate tensile strength	Elongation		Reduction of area
			2-inch	8-inch	
	Lbs./in.[3]	*Lbs./in.*[3]	*Per cent*	*Per cent*	*Per cent*
AHPF3	33,600	44,150	(1)	(1)	(2)
AHPF3	32,800	44,600	15.0	11.0	14.5
AHPM3	30,500	43,000	13.5	10.5	14.0
AHPM3	31,600	43,050	12.0	8.0	14.0
AHPB3	31,500	43,000	13.0	9.5	14.5
AHPB3	32,400	46,150	18.0	14.0	15.3
AHPF4	31,250	42,000	11.0	7.5	10.0
AHPF4	33,650	41,700	8.5	4.5	9.0
AHPM4	29,500	37,500	6.0	4.5	10.0
AHPM4	34,250	44,250	9.0	5.0	9.5
AHPB4	33,400	42,700	(1)	(1)	10.5
AHPB4	32,000	44,350	15.0	9.0	14.5
Average	31,830	41,480	12.6	7.7	12.6

[1] Broke in fillet.

[2] Broke outside of gage points.

TABLE 8.—*Tensile properties of 1-inch wrought-iron pipe, as determined on full-size specimens*

[A=iron made by Aston process; HP=hand-puddled iron; AHP=composite iron containing equal amounts of A and HP; x and y indicate the two ends of the pipe length from which specimens were cut]

Designation of material	Tensile properties [1]		
	Yield point	Breaking load	Elongation (8-inch)
	Pounds	*Pounds*	*Per cent*
A1x	17,050	25,100	17.0
A1y	17,200	24,600	18.0
A2x	17,400	24,850	13.0
A2y	17,700	25,000	16.0
A3x	-------	24,150	11.5
A3y	17,400	24,550	13.0
Average	17,350	24,700	14.7
HP1x	-------	26,900	12.0
HP1y	19,000	25,700	8.0
HP2x	-------	27,300	13.0
HP2y	18,700	26,850	13.0
HP3x	19,900	27,550	13.0
HP3y	19,650	27,700	12.5
Average	19,300	27,000	11.9
AHP1x	19,000	25,650	9.5
AHP1y	-------	24,550	8.5
AHP2x	18,750	25,400	9.0
AHP2y	-------	25,700	8.5
AHP3x	18,300	25,750	10.5
AHP3y	-------	25,000	(2)
Average	18,700	25,350	9.2

	Average tensile properties [2]	
	Yield point	Ultimate tensile strength
	Lbs./in.	*Lbs./in.*
A	33,150	47,250
HP	36,900	51,600
AHP	35,700	48,450

[1] A Riehle testing machine 100,000-pound capacity was used; yield point was determined by drop of beam.

[2] Broke outside of gage marks

In many specifications for pipe the tensile properties may be determined on strips cut from the pipe instead of on full-size pipe specimens. Although it is usually intended that the strip method shall apply only to pipe of relatively large diameter, it is sometimes used for pipe of small diameter. It was considered of interest, therefore, to determine the tensile properties of the three types of pipe on longitudinal strips machined from the pipe. Eighteen-inch specimens were machined without any flattening of the pipe, so that the edges were parallel (not radial). The width in the shoulders was 2 inches and in the central portion, over a length of 10 inches, the width was 1 inch. The specimens were tested in an Amsler machine, special grips being used so as to maintain the original curvature throughout the test. It will be noted, by comparing the results (Table 9) with those in Table 8, that the most marked effect produced by using specimens of this form was the lowering of the elongation.

(2) TORSIONAL PROPERTIES.—Torsion tests were made on four specimens of each of the three kinds of pipe. The specimens for the tests, which were carried out in a Riehle torsion testing machine of 60,000-pounds capacity, were 44 inches in length and the ends were plugged as in the tension tests of pipe. The length of the specimen between grips was 38 inches. The results obtained are summarized in Table 10 and the appearance of the pipe after testing is shown in Figure 8.

TABLE 9.—*Tensile properties of 1-inch wrought-iron pipe determined on longitudinal strips machined from the pipe*

[A=iron made by Aston process; HP=hand-puddled iron; AHP=composite iron containing equal parts of A and HP]

Material	Tensile properties		
	Yield point	Ultimate tensile strength	Elongation (8-inch)
	Lbs./in.²	*Lbs./in.²*	*Per cent*
A	36,300	49,200	9.0
	33,400	47,350	8.0
	36,650	51,750	12.0
	33,700	48,250	9.6
	35,700	50,600	11.5
	35,150	49,500	10.0
Average	35,150	49,440	10.0
HP	37,500	52,250	8.8
	35,900	51,150	9.8
	38,500	52,050	7.0
	45,750	52,800	7.5
	39,850	56,100	13.1
	40,750	55,100	9.9
Average	39,700	53,240	8.9
AHP	36,100	50,300	8.0
	36,150	49,900	5.7
	38,100	51,850	7.0
	34,100	48,750	9.5
	38,950	49,900	5.0
	37,400	51,350	6.8
Average	36,800	50,340	7.0

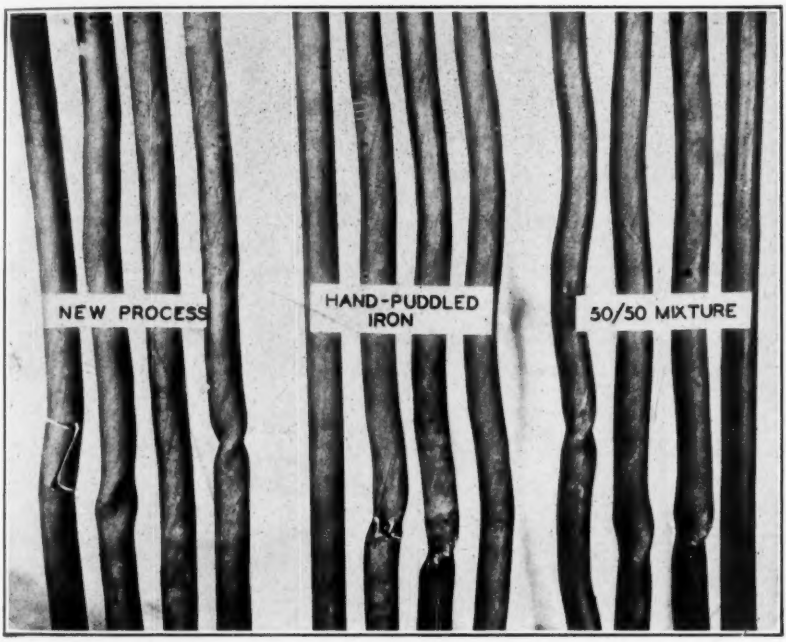

FIGURE 8.—*Appearance of the pipe after the torsion test*

TABLE 10.—*Torsional properties of 1-inch wrought-iron pipe*

[A=iron made by Aston process; HP=hand-puddled iron; AHP=composite iron containing equal parts A and HP]

Material	Torsional properties			
	Yield point [1]	Maximum moment	Total number of 360° twists	
	In./lbs.	*In./lbs.*	°	*Turns*
A1	6,000	9,850	1,260	3.5
A2	6,000	10,700	1,465	4.07
A3	5,900	10,300	1,340	3.72
A4	6,000	10,750	1,380	3.83
Average	5,975	10,395	1,361	3.78
HP1	6,550	11,250	755	2.09
HP2 [2]	7,000	9,600	380	1.05
HP3	6,800	11,650	1,170	3.25
HP4	6,850	11,450	1,180	3.27
Average	6,800	10,985	871	2.42
AHP1	5,000	10,450	1,260	3.50
AHP2	6,000	11,100	1,450	4.03
AHP3 [2]	5,600	9,850	810	2.25
AHP4	5,650	10,750	1,500	4.16
Average	5,560	10,540	1,255	3.48

[1] By drop of beam.

[2] The weld parted at the load end during the test.

(3) FLATTENING TESTS.—Six specimens, each 6 inches long, of each of the three kinds of wrought-iron pipe were used in the flattening tests. The load was applied perpendicularly along the entire length of the specimen and at 90° to the weld. Table 11 contains the results of the tests.

TABLE 11.—*Results of flattening tests of 1-inch wrought-iron pipe*

[A=iron made by Aston process; HP=hand-puddled iron; AHP=composite iron containing equal parts of A and HP]

Material	Maximum load	Remarks
	Pounds	
A1	9,150	All fractures were fibrous, no defective welds revealed.
A1	9,150	
A2	8,950	
A2	9,000	
A3	8,200	
A3	9,100	Not across the weld.
Average	8,925	
HP1	9,900	All fractures were fibrous, no defective welds revealed.
HP1	10,000	
HP2	10,400	
HP2	10,500	Not across the weld.
HP3	10,000	
HP3	10,050	
Average	10,140	
AHP1	9,600	All fractures were fibrous, no defective welds revealed.
AHP1	10,050	
AHP2	9,500	
AHP2	9,300	
AHP4	), 975	
AHP4	9,950	
Average	9,790	

(b) 1-INCH ROUNDS

The 1-inch rounds used were not available as a commercial product and were made especially for this study. In addition to tension and torsion tests which were also made on the pipe materials, several other mechanical tests which can not be carried out readily on pipe or on flat strips were made.

(1) TENSILE PROPERTIES.—The tensile properties of the wrought iron made by the new process in the form of 1-inch rounds were

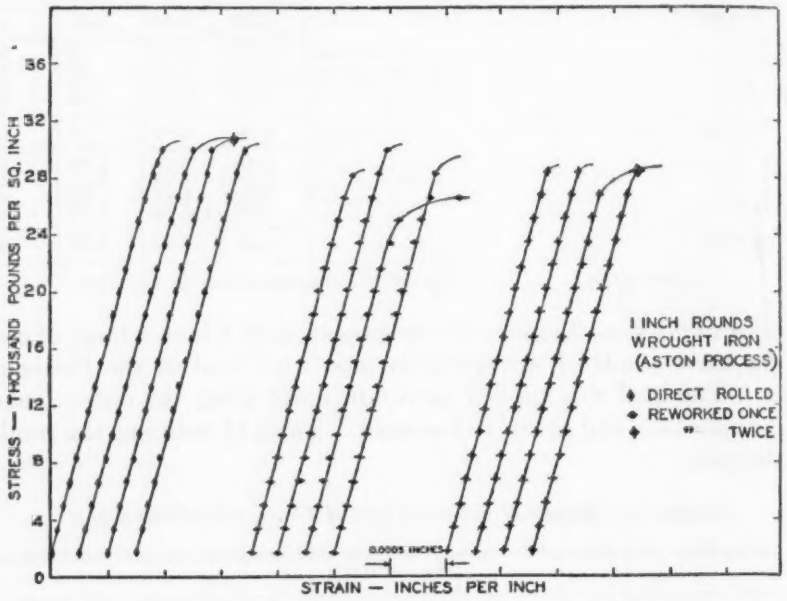

FIGURE 9.—*Stress-strain curves of wrought iron made by the Aston process in 1-inch rounds tested in tension*

determined on both the full-size bar and on specimens machined from the bar. The results are summarized in Table 12. In the case of the machined specimens, strain measurements were made by means of the Ewing extensometer and the curves summarizing these results are given in Figure 9. It is very evident from the results obtained that the tensile properties of the iron were only slightly changed by the "refining" given the material before rolling into the form of 1-inch rounds. The tensile strength was lowered slightly and the elongation increased somewhat as the amount of working given the material was increased.

TABLE 12.—*Tensile properties of wrought iron made by the Aston process rolled into the form of 1-inch rounds*

TESTS MADE ON FULL-SIZE BARS, 18 INCHES LONG

Specimen	Material	Tensile properties				
		Yield point [1]	Ultimate tensile strength	Elongation		Reduction of area
				2-inch	8-inch	
		Lbs./in.²	*Lbs./in.²*	*Per cent*	*Per cent*	*Per cent*
1aa	Rolled directly from billet to 1-inch round	27,750	49,050	40.0	27.5	47.4
1bb		28,600	48,650	----------	25.0	48.1
1cc		28,700	49,250	[2]	[2]	[2]
1dd		29,300	50,000	44.0	27.5	45.3
	Average	28,590	49,240	42.0	26.7	46.9
2aa	"Single refined"	28,150	48,850	47.0	30.0	50.7
2bb		28,550	48,650	49.0	31.5	50.4
2cc		28,550	49,150	49.0	29.3	50.9
2dd		28,550	49,000	47.0	30.0	49.5
	Average	28,450	48,910	48.0	30.2	50.4
3aa	"Double refined"	27,300	48,050	45.0	29.5	51.9
3bb		27,650	47,900	50.0	31.5	51.5
3cc		28,100	48,400	49.5	30.3	50.7
3dd		28,800	48,200	[3]	[3]	53.1
	Average	27,960	48,140	48.2	30.4	51.8

TESTS MADE ON BARS MACHINED TO 0.875-INCH DIAMETER, 8-INCH GAGE LENGTH

1a	Rolled directly from billet to 1-inch round	29,850	49,750	44.0	28.5	47.3
1b		30,500	50,250	43.5	29.0	47.9
1c		30,700	50,250	44.0	27.5	46.6
1d		29,850	49,950	43.0	30.0	48.1
	Average	30,220	50,050	43.6	28.7	47.5
2a	"Single refined"	28,200	48,550	46.0	30.5	50.0
2b		29,850	48,150	46.0	30.5	49.2
2c		28,200	47,900	45.0	29.0	50.7
2d		28,200	48,100	46.0	30.0	49.8
	Average	28,610	48,175	45.7	30.0	50.0
3a	"Double refined"	28,700	43,450	49.0	29.5	51.1
3b		29,000	43,350	43.5	28.5	46.9
3c		28,700	48,500	45.0	29.0	48.3
3d		28,200	47,750	46.0	29.5	50.3
	Average	28,650	48,260	45.9	29.1	49.1

[1] By stress graph drawn by the Amsler machine.
[2] Broke in jaws of the machine, outside of gage marks.
[3] Broke outside of gage marks.

(2) TORSIONAL PROPERTIES.—Torsion tests of the 1-inch round material were carried out on specimens 15 inches long, the central portion of which had been machined to a diameter of one-half inch over a 10-inch gage length. The results are given in Table 13, and in Figure 10 are given curves showing the behavior of the iron when stressed in torsion. It will be seen that there was no pronounced change in the torsional properties produced by the refining given the iron. This observation is in agreement with the results of the tension tests.

(3) IMPACT RESISTANCE.—The resistance to impact of the iron in the form of notched specimens (notched-bar impact resistance) was determined by two methods, viz, resistance to repeated blows (Eden-

Foster test) and resistance to a single blow (Izod test). The results (Tables 14 and 15), in general, indicate no marked difference in the notched-bar single-blow impact resistance resulting from the extra mechanical working which some of the material received. In the case of the repeated-blow tests, however, the average impact resist-

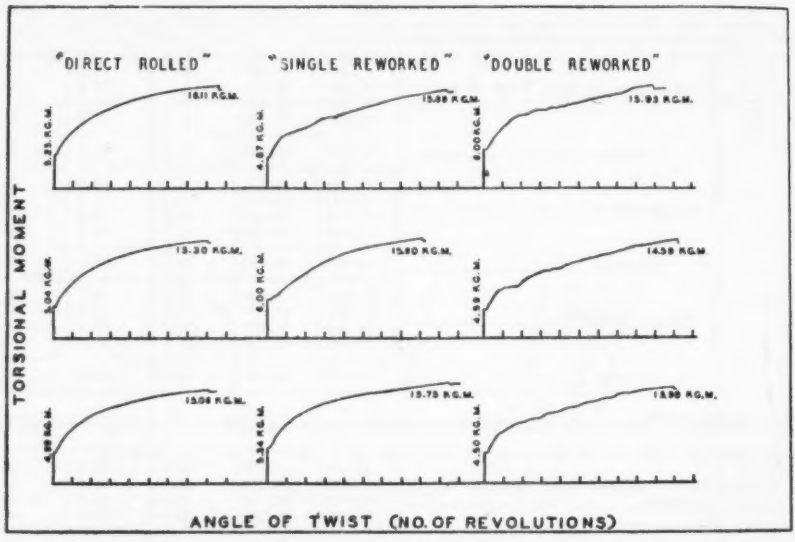

FIGURE 10.—*Stress-strain curves of wrought iron made by the Aston process in 1-inch rounds tested in torsion*

ance was somewhat improved by the double refining given to some of the iron. In all cases the conventional test specimens were machined out of the 1-inch round, the full-size bar was not used.

TABLE 13.—*Torsional properties of wrought iron made by the Aston process rolled into the form of 1-inch rounds*

Specimen No.	Material	Torsional properties		
		Yield point	Maximum moment	Twist (number of 360° twists)
		Ft./lbs.	*Ft./lbs.*	
1a	Rolled directly from billet to 1-inch round	39.0	119.5	9.64
1b		33.0	109.0	8.30
1c		38.0	116.5	8.80
1d		36.5	110.5	8.13
	Average	36.6	114.0	8.72
2a	"Single refined"	47.5	120.0	10.34
2b		38.5	114.0	9.60
2c		35.0	113.5	9.50
2d		33.0	105.5	10.33
	Average	38.5	113.2	9.95
3a	"Double refined"	40.0	.....	.....
3b		32.5	110.5	10.15
3c		43.5	113.0	8.35
3d		33.0	105.5	10.35
	Average	37.2	109.7	9.61

TABLE 14.—*Repeated-blow notched-bar impact resistance of wrought iron made by the Aston process rolled to the form of 1-inch rounds*

[Eden-Foster test. Specimens were 6½ inches long and one-half inch diameter, with a round filleted notch 0.05 inch deep. A 2-pound hammer with a 4-inch drop was used]

Specimen	Material	Impact resistance 2-pound hammer, 4-inch drop
		Number of blows
1a	Rolled directly from billet to 1-inch round	3,114
1b		2,836
1c		3,578
1d		3,080
	Average	3,152
2a	"Single refined"	3,138
2b		3,166
2c		3,128
2d		3,342
	Average	3,193
3a	"Double refined"	3,400
3b		3,100
3c		3,346
3d		3,456
	Average	3,325

TABLE 15.—*Single-blow notched-bar impact resistance of wrought iron made by the Aston process rolled to the form of 1-inch rounds*

[Izod test. Triple-notch specimens (1 cm[1] (0.394 by 0.394 inch), section, 45° V notch, 0.079 inch deep) were used, the notches being arranged 90° apart on three sides of the specimen. Capacity of Izod pendulum machine 120 ft./lbs.]

Specimen	Material	Impact resistance energy absorbed [1]		
		a	b	c [2]
		Ft./lbs.		
1a	Rolled directly from billet to 1-inch round	51.5	44.5	57
1b		55	52	51.5
1c		53	57	46
1d		50	53	51
1e		57	53	52
1f		55	56	47
1g		50	50	57
1h		61	54.5	57
	Average			52.6
2a	"Single refined"	52	52	51
2b		55.5	55	52
2c		51	52	50
2d		50	55	45
2e		43	42	45
2f		50	51	50
2g		50	55	50
2h		50	47	45
	Average			49.6
3a	"Double refined"	55		
3b		53	53	53
3c		50.5	43	50
3d		56.5	58	48
3e		48	46	51.5
3f		52	52.5	49
3g		53	55	45.5
3h		56	55	44.5
	Average			51.3

[1] None of the specimens fractured completely upon impact.
[2] a, b, and c indicate the three notches on each specimen.

4. CORROSION RESISTANCE

(a) LABORATORY CORROSION TEST

The relative corrosion resistance of the three wrought irons in the form of pipe was studied by laboratory tests carried out in tap water and in a 3½ per cent (by weight) sea-salt solution. The results of such tests, of course, are not necessarily indicative of the behavior of the materials in service. However, under service conditions which approximate in most respects the essential conditions of the tests, the service behavior of materials would be expected to follow the indications of the test results. Short pieces of the three kinds of pipe, varying from 1¼ to 1¾ inches in length, were used as specimens. The sawed ends of samples were ground smooth on an emery wheel and the samples were then cleaned free from grease by hot soapsuds, rinsed in hot water, dried and weighed. No attempt was made to remove adhering scale; for example, by pickling, as it was desired to test the materials in a condition approaching as nearly as possible the commercial condition.

The tests carried out in both solutions consisted of the following: (*a*) Immersion in the still liquid without any (intentional) aeration, (*b*) immersion in the liquid through which air was passed, and (*c*) repeated immersion or "wet-and-dry" test. The ends of most of the specimens, after weighing, were covered with a coating of aluminum-pigmented "rubber cement" (thermoprene). It was noticed, however, after 24 hours' exposure that there was evidence of some corrosion on the ends and, since no marked difference was noted in the behavior of these samples and of those in which the ends were left bare, it may be concluded that the corrosion losses observed represent the attack on the cut ends as well as on the surfaces of the pipe. Twelve specimens from each of the three kinds of pipe (four specimens from three different pipe lengths) were tested in the two liquids with each of the three testing methods given above.

In carrying out the simple immersion tests, without aeration, eight samples, in two sets of four placed end to end and held in place by means of glass rods extending through the pipe, were immersed in the liquid to a depth of approximately 3 inches. Large glass battery jars were used as containers (fig. 11), and water was added from time to time to maintain the initial volume (4 liters) of the liquid. In carrying out the immersion tests, with aeration, the samples were placed end to end within a rubber tubing (inside tube of a bicycle tire), the whole being immersed in the liquid in a large container. Air was bubbled slowly through the inside of the assembled specimens during the daytime (eight hours). The repeated immersion or "wet-and-dry" tests were carried out by means of the apparatus shown in Figure 12, a rather complete description of which has already been

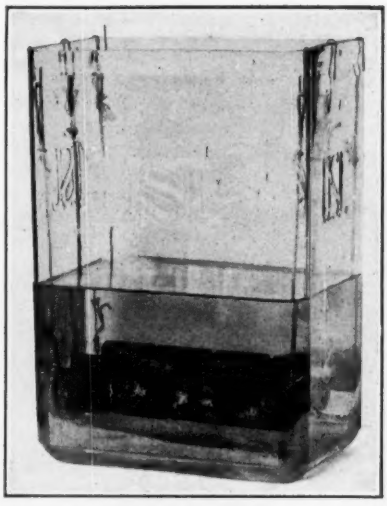

FIGURE 11.—*Simple immersion method of carrying out the corrosion tests in unaerated solutions*

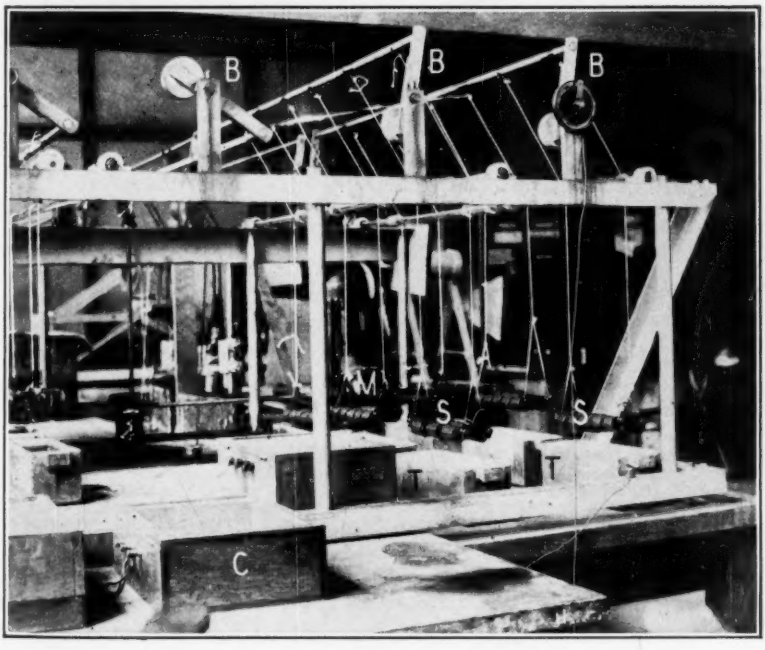

FIGURE 12.—*Apparatus used for the wet-and-dry corrosion tests*

By means of the clock, *C*, the motor, *M*, is started at 15-minute intervals. The bell cranks, *B*, are turned and the specimens, *S*, are dipped into the solution in the tanks, *T*, and then raised into the air.

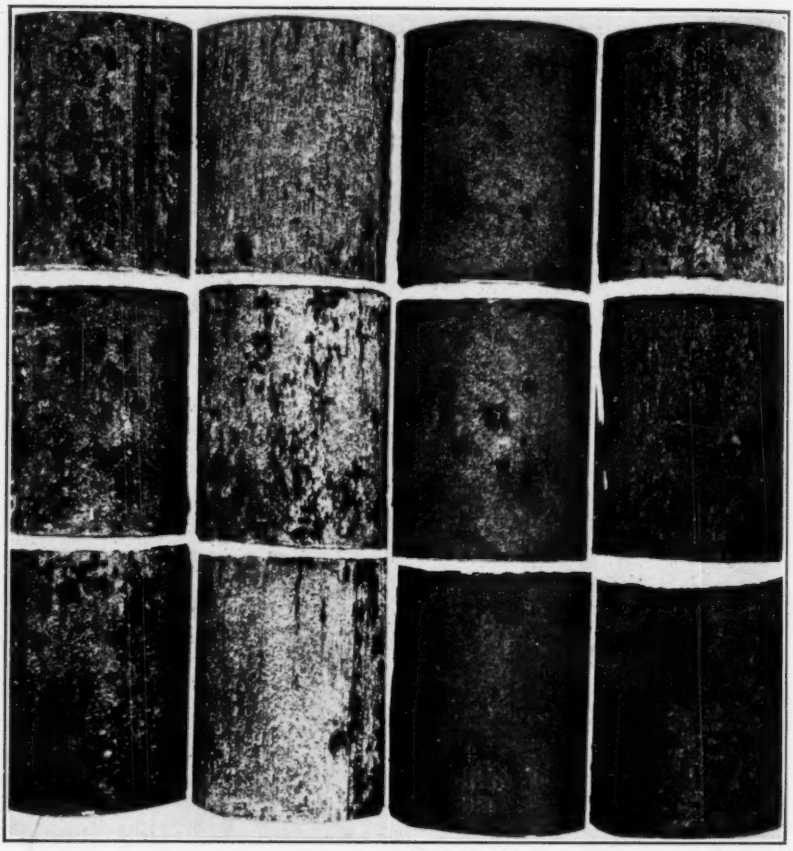

FIGURE 13.—*Appearance of the outer surface of wrought-iron pipe after corrosion*

The pipe in the upper horizontal row is hand-puddled wrought iron; that in the middle row, new-process iron; and that in the third, the composite iron made from equal amounts of the other two. The specimens in the first vertical row at the left were corroded by simple immersion in tap water; those in the next, by immersion in 3½ per cent sea-salt solution; those in the third row, by the wet-and-dry method in tap water; and those in the right-hand row, by the wet-and-dry method in sea-salt solution.

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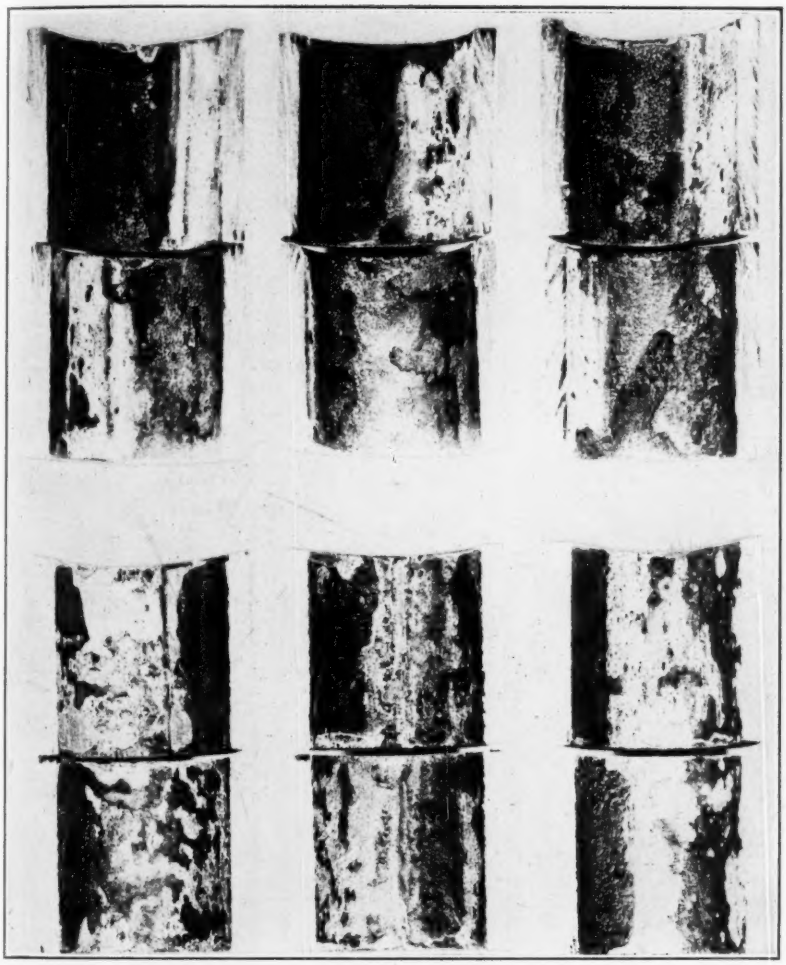

FIGURE 14.—*Appearance of the inner surface of wrought-iron pipe after corrosion by immersion in aerated solutions*

Each group of two represents the two halves of the specimen split lengthwise. The specimens are arranged in vertical rows according to the kind of iron as follows (beginning at the left): New-process iron, composite iron, hand-puddled iron. The specimens in the upper double row were corroded in sea-salt solution, those in the lower double row in tap water.

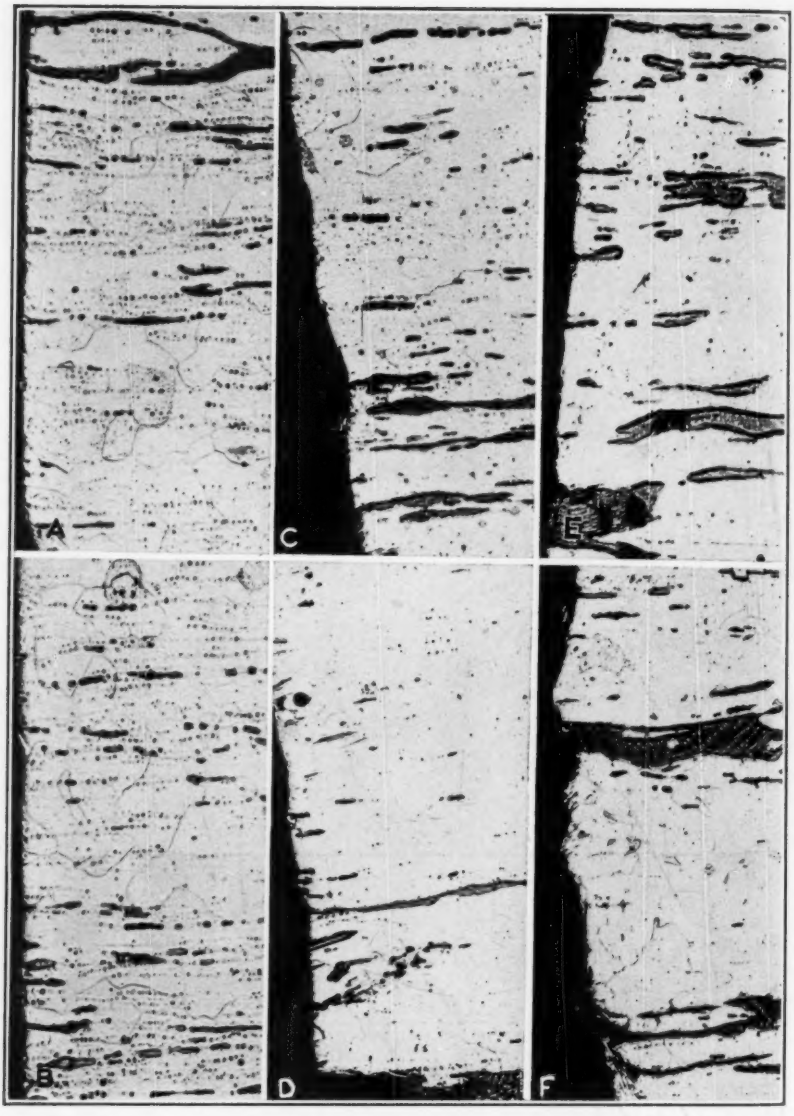

FIGURE 16.—*Relation of the corrosive attack on "cut" ends of wrought-iron pipe, after simple immersion, to the microstructure,* × *100, reduced to* × *75*

The micrographs represent longitudinal sections of the pipe at the corroded end, which is shown at the left in each case. *a, b,* New-process iron in tap water and 3½ per cent sea salt solution, respectively; *c, d,* hand-puddled iron in tap water and 3½ per cent sea-salt solution, respectively; *e, f,* the composite iron in tap water and 3½ per cent sea-salt solution, respectively.

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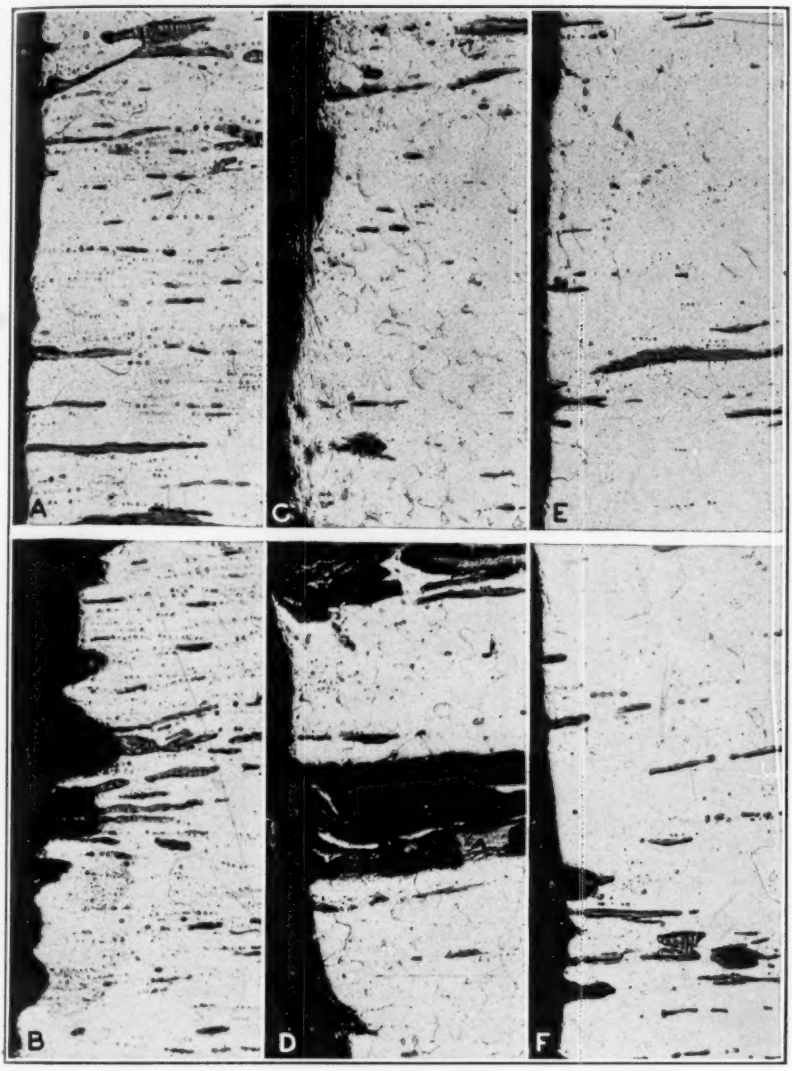

FIGURE 17.—*Relation of the corrosive attack on "cut" ends of wrought-iron pipe after immersion in aerated solutions, to the microstructure, × 100, reduced to × 75*

The micrographs represent longitudinal sections of the pipe at the corroded end, which is shown at the left in each case. *a, b,* New-process iron in tap water and 3½ per cent sea-salt solution, respectively; *c, d,* hand-puddled iron in tap water and 3½ per cent sea-salt solution, respectively; *e, f,* the composite iron in tap water and 3½ per cent sea-salt solution, respectively.

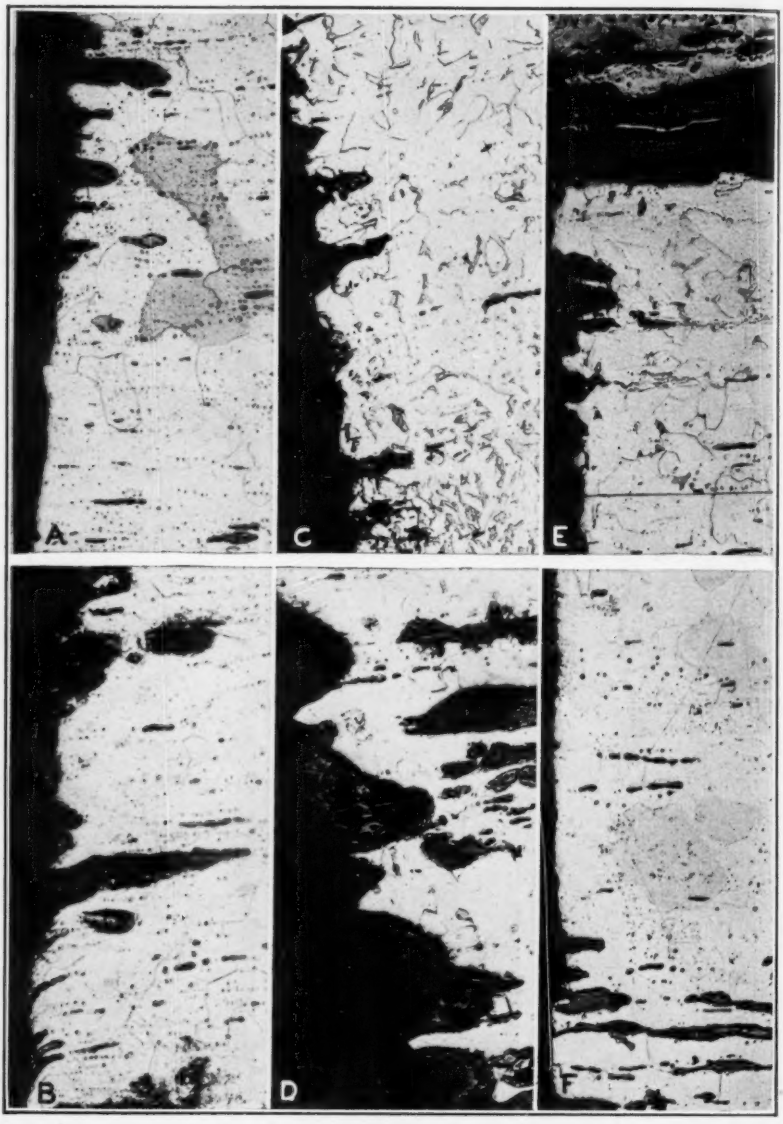

FIGURE 18.—*Relation of the corrosive attack on "cut" ends of wrought-iron pipe after corrosion by the wet-and-dry method, to the microstructure, × 100, reduced to × 75*

The micrographs represent longitudinal sections of the pipe at the corroded end, which is shown at the left in each case. *a, b,* New-process iron in tap water and 3½ per cent sea-salt solution, respectively; *c, d,* hand-puddled iron in tap water and 3½ per cent sea-salt solution, respectively; *e, f,* the composite iron in tap water and 3½ per cent sea-salt solution, respectively.

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published.[8] The specimens, which were supported by cords and glass rods as shown, were wet at 15-minute intervals with the liquid (tap water or sea-salt solution) by being dipped momentarily into the solution and then raised into the air. The specimens were immersed in the liquid approximately one minute at each immersion. The corrosion tests were allowed to continue for three months (92 days) except in the case of a few specimens which were examined at the end of 2 months. No attempt was made to remove the corrosion product during the period of corrosion. The tests were carried out during the three summer months at room temperature. At the end of the 3-month period the specimens were cleaned free from the corrosion product, washed first in hot water, and then in alcohol, dried, and weighed. The loss of weight per unit of surface area was used as a basis of comparison.

No marked or important difference in the character of the corrosion product on the different kinds of iron was noted. The character of the corrosion product differed decidedly, however, according to the conditions under which the corrosive attack had occurred. A loose flocculent deposit which could be removed very readily was formed on the specimens which were corroded by simple immersion (unaerated) in both tap water and salt solution. The deposit which formed on the specimens corroded in the aerated solutions was much more adherent, but was readily removed by means of a bristle brush. In the case of the wet-and-dry tests, however, the character of the scale formed was decidedly different from that in the other tests and was removed only with difficulty. On the specimens corroded in sea-salt solution the scale, though much more adherent than in the other cases, was coarse and was removed by vigorous brushing. The scale on the specimens corroded by repeated immersion in tap water, however, though thin, was smooth and very adherent. It was removed with a bristle brush only with great difficulty even after the specimens had been allowed to remain in a 10 per cent (by weight) solution of ammonium citrate for two days. The appearance of the outer and inner corroded surfaces of representative specimens of the various tests is shown in Figures 13 and 14, respectively.

A summary of the average corrosion loss of the three kinds of pipe when corroded in different ways in tap water and in salt solution is given in Table 16 and a graphical summary of the results of the corrosion tests in Figure 15. As shown by the data in Table 16, there appears to be a very slight difference in the corrosion rate of the hand-puddled and the new-process wrought iron in favor of the hand-puddled product. It is also very apparent that the method by which the attack is brought about is a much more important

[8] H. S. Rawdon and E. C. Groesbeck, Effect of the Testing Method on the Determination of Corrosion Resistance, B. S. Tech. Paper No. 367; 1928.

factor in determining the corrosion resistance than is any difference in the character of the iron resulting from the process by which it has been prepared. The appearance of the corroded specimens shown in Figures 13 and 14 is typical of results obtained with the different materials corroded under different conditions. Corrosion on the cut ends of wrought iron in the form of pipe or bar is

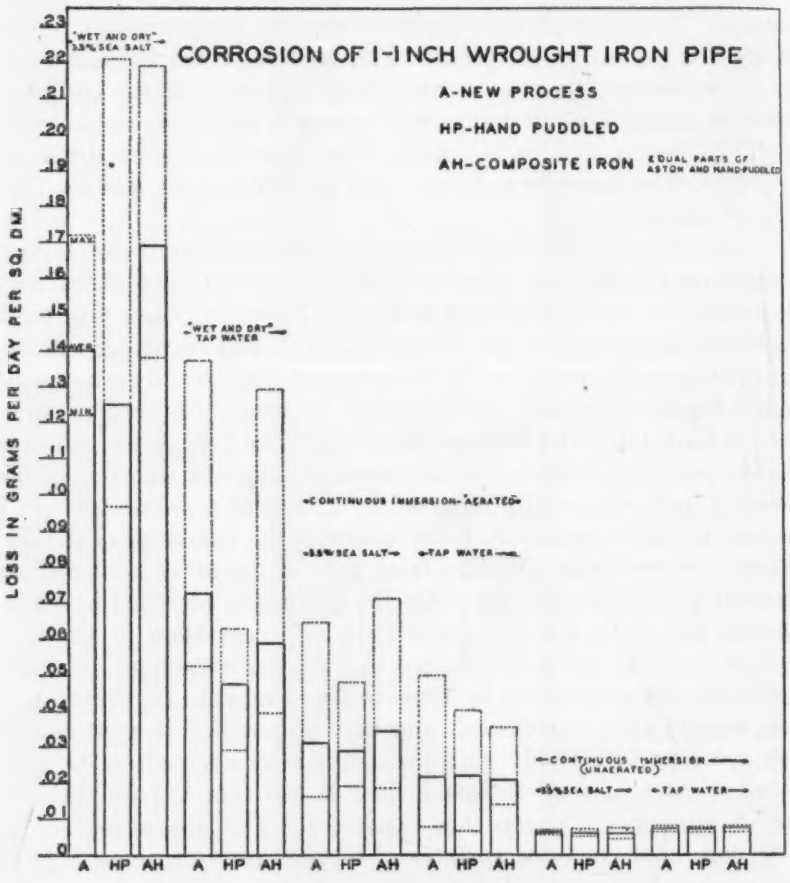
CORROSION OF 1-INCH WROUGHT IRON PIPE
A-NEW PROCESS
HP-HAND PUDDLED
AH-COMPOSITE IRON EQUAL PARTS OF ASTON AND HAND-PUDDLED
LOSS IN GRAMS PER DAY PER SQ. DM.
"WET AND DRY" 3.5% SEA SALT
"WET AND DRY" TAP WATER
CONTINUOUS IMMERSION-AERATED
3.5% SEA SALT
TAP WATER
CONTINUOUS IMMERSION (UNAERATED)
3.5% SEA SALT
TAP WATER
A HP AH A HP AH A HP AH A HP AH A HP AH A HP AH A HP AH

FIGURE 15.—*Summary of the results of the corrosion tests*
The maximum and minimum values are shown by the dotted lines.

generally conceded to be more severe than on the rolled surface of the same material. The character and extent of the corrosive attack on the cut ends of some of the specimens used in the present tests are shown in Figures 16, 17, and 18. These micrographs are further confirmation of the conclusion based upon the other corrosion data that the conditions under which the corrosive attack occurred played a greater part in determining the corrosion loss than did differences in the material itself.

TABLE 16.—*Average*[1] *corrosion losses of wrought-iron pipe in accelerated laboratory tests of three months' duration*

[A=iron made by the Aston process; HP=hand-puddled iron; AHP=composite iron containing equal amounts of A and HP]

Material	Corrosion method					
	Simple immersion		Immersion aerated		"Wet-and-dry"	
	Sea-salt solution[2]	Tap water	Sea-salt solution[2]	Tap water	Sea-salt solution[2]	Tap water
A	[3] 0.0063	0.0074	0.031	0.0215	0.140	0.073
HP	.0061	.0072	.029	.0217	.125	.047
AHP	.0059	.0077	.034	.0207	.168	.057

[1] See fig. 15 for the range of the determinations.
[2] 3½ per cent solution, by weight.
[3] g/dm²/day.

(b) ELECTROLYTIC SOLUTION POTENTIAL

Coincident with the laboratory corrosion tests and before the results of these tests were known, a few simple tests were carried out to show the relative behavior of the two wrought irons when in electrical contact with each other and immersed in a solution. Small pieces of the skelp strip, 3 by ¾ inch, were used as specimens. These were cleaned by pickling, after which they were heated in an oven to approximately 200° C. in order to drive off any hydrogen present. A copper wire was firmly attached to one end of the specimen and the junction of iron and copper, as well as the wire itself, coated with paraffin. A dilute solution of sodium sulphate (1 per cent, by weight) was used as the electrolyte in which the two iron specimens were immersed, "face to face," slightly more than 1 inch apart. A small potentiometer of the portable type was used to show the magnitude and direction of the e. m. f. which resulted when electrical contact was established between the two specimens.

There was considerable variation in the e. m. f. observed for several different couples as well as for the same couple used on different days, which is not surprising in view of the simple method used. The results were consistent, however, in one respect. The hand-puddled iron was, in all cases, the cathode of the couple; that is, for the conditions used, the "solution pressure" of the new-process iron was slightly higher than that of the comparison material.

5. STRUCTURAL EXAMINATION

Inasmuch as the structural condition of wrought iron is one of its most characteristic features, the comparison of the structure of the two types of iron was carried out in considerable detail.

(a) PIPE MATERIALS

(1) BALL.—In Figures 19 and 20 is shown the appearance of portions of a wrought-iron ball as taken from the hand-puddling furnace and of a ball of the wrought iron made by the new process as it comes from the shotting cup. Only a very small portion of the entire ball is shown in either case. The microstructure of the two irons was examined on a considerable number of fragments in order to obtain a good idea of the average structure. Figures 21 and 22 are representative of the conditions found. Figure 21 (*a*) and (*b*) represents the average condition of the hand-puddled iron with respect to slag distribution. After etching, evidence of the presence of carbon was frequently found. The metal was quite "patchy" in this respect. The condition shown in micrograph (*b*) is not unusual. Patches with a carbon content as high as that shown in (*c*) (fig. 21) appeared to be not uncommon and occasionally patches of iron in which the carbon was considerably above 1 per cent were found (fig. 21 (*d*)). The structural condition of the new-process iron in the ball was much more uniform than that of the hand-puddled iron with which it was compared. The degree to which the continuity of the iron matrix was broken up during the shotting operation and the slag was mechanically incorporated with the iron is surprising. In addition to the coating of slag covering the globules of iron formed by the shotting operation, the interior of globules showed an intimate mixture of the slag often suggestive of a dendritic arrangement (fig. 21 (*b*)). No evidence of the presence of carbon was found upon etching and the structure in this respect afforded a striking contrast to the other type of iron.

(2) MUCK BAR.—In Figure 23 is shown the microscopic appearance of the two irons after being rolled into muck bar. The less uniform condition of the hand-puddled iron, as shown by the larger slag areas and the presence of the "carbon streaks," which were revealed by etching polished sections, is evident. The microstructure of the muck bar, as shown in Figures 24, 25, and 26, was found to be in agreement with that of the ball. The hand-puddled iron showed occasional slag streaks which were considerably larger than any found in the other iron and streaks of metal with a rather high carbon content were not uncommon. No carbon streaks were found in the muck bar of the new-process wrought iron and the average distribution of the slag threads was considered to be somewhat more uniform. In the comparison of the two irons, here and elsewhere, the examination of transverse sections was used more than longitudinal sections, since a transverse section gives a much better index of the distribution of the slag streaks than the other does.

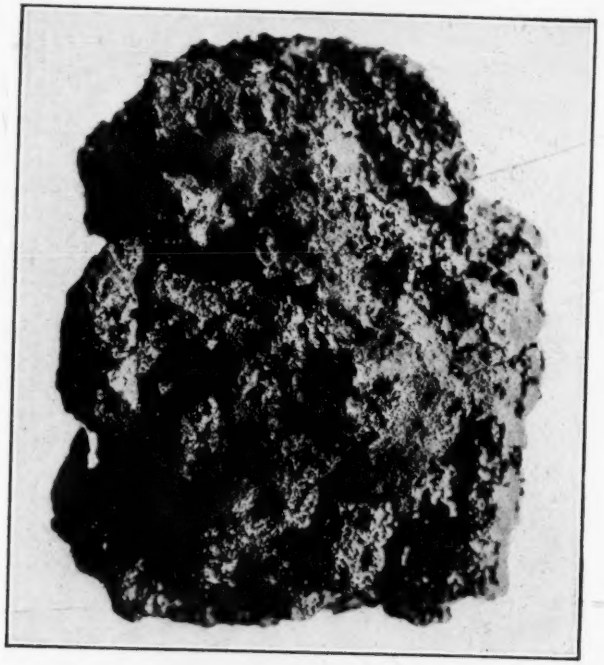

FIGURE 19.—*Portion of a ball of hand-puddled wrought iron,* × ½

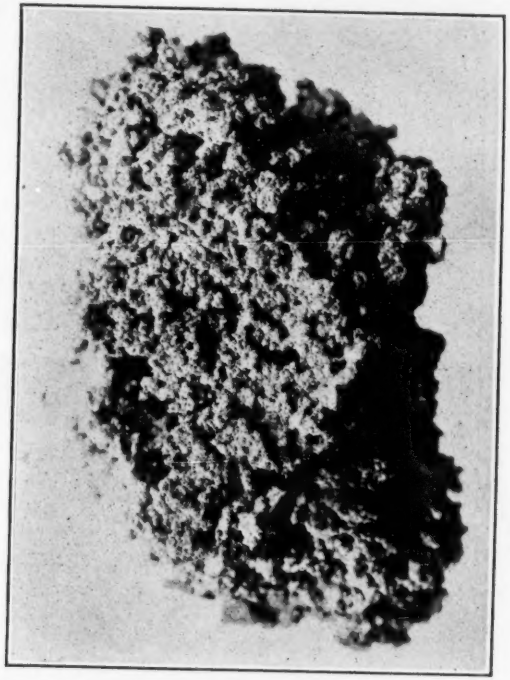

FIGURE 20.—*Portion of a ball of iron made by the Aston process,* × ½

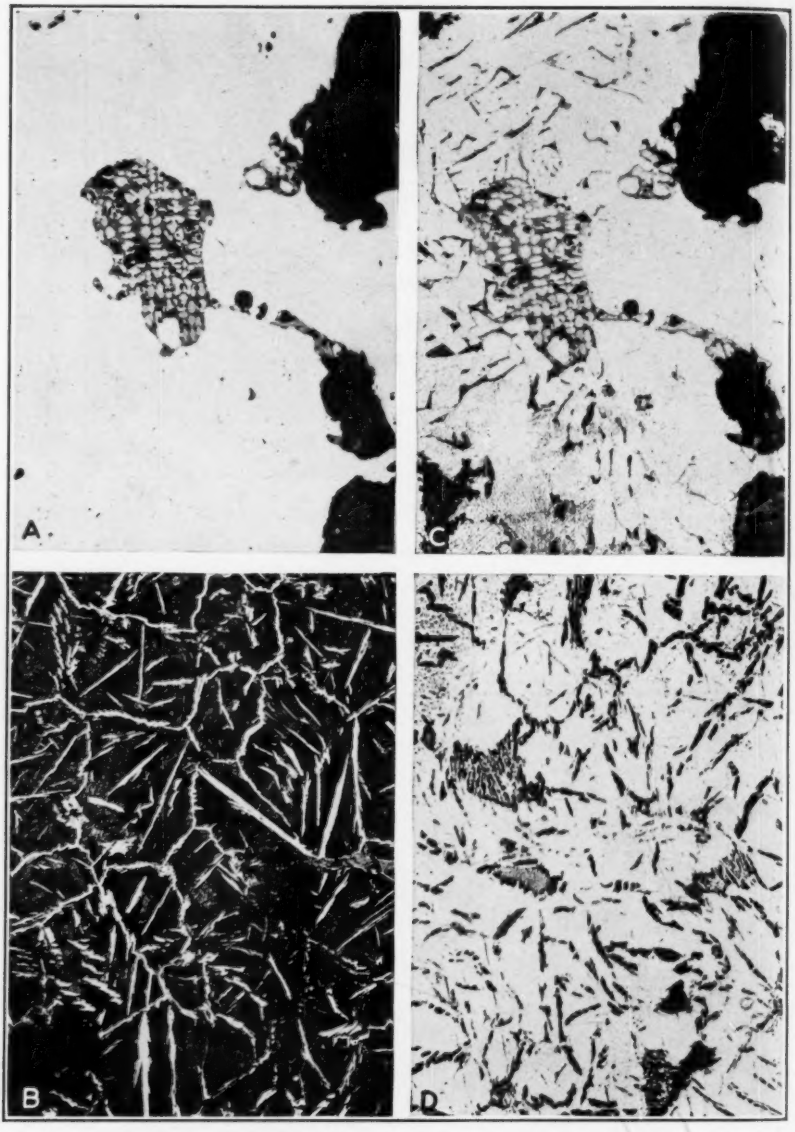

FIGURE 21.—*Microstructure of hand-puddled iron in the ball stage,* $\times$ *100, reduced to* $\times$ *75*

a, Unetched section, typical of the structure of much of the ball; *b*, same, etched with picric acid solution. Note the carbon in the form of small islands of pearlite; *c*, portion of the same ball having a carbon content over 1 per cent, etched with picric acid solution; *d*, another portion of the same ball showing a high carbon content, etched with hot alkaline sodium picrate solution.

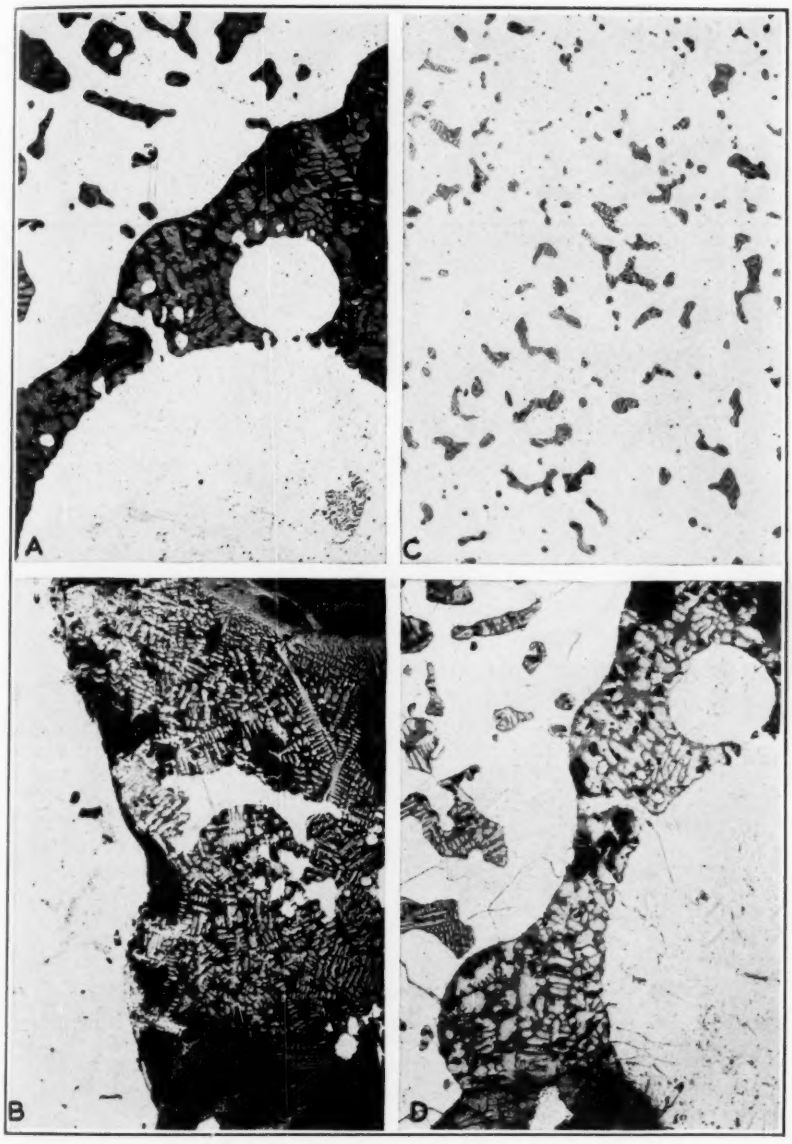

FIGURE 22.—*Microstructure of wrought iron made by the new process, in the ball stage, × 100, reduced to × 75*

a, *b*, and *c* represent areas from two different balls, unetched. Micrograph *c* shows the intimate mixture of slag and iron within what may appear to be a solid lump of metal, and *d*, same area as *a*, etched with picric acid solution. No carbon was revealed.

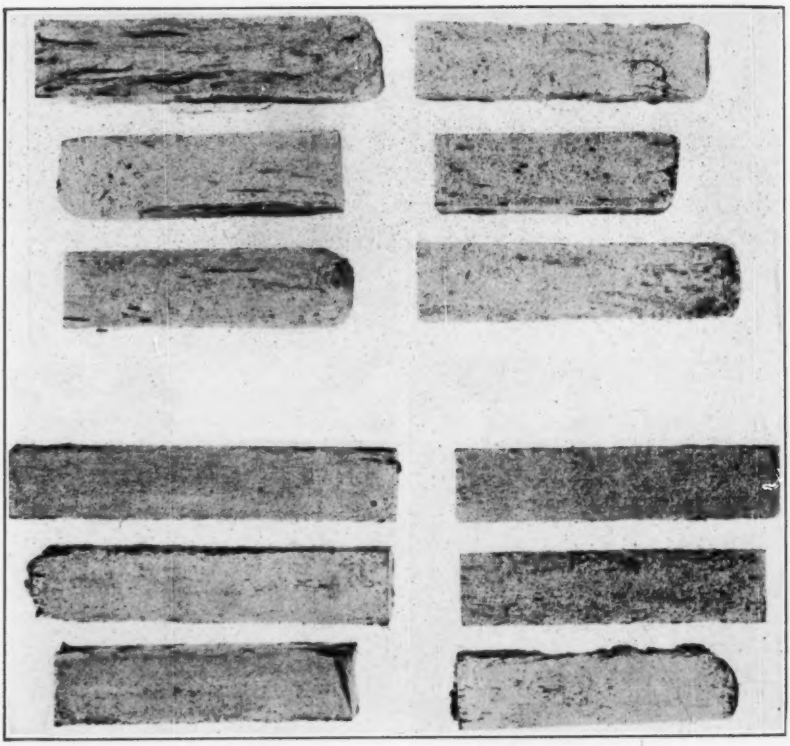

FIGURE 23.—*Microstructure of wrought iron in the muck-bar state,* × 2/3

The upper group represents different samples of hand-puddled iron; the lower, corresponding samples of the new-process iron. Etchant, 4 per cent nitric acid solution.

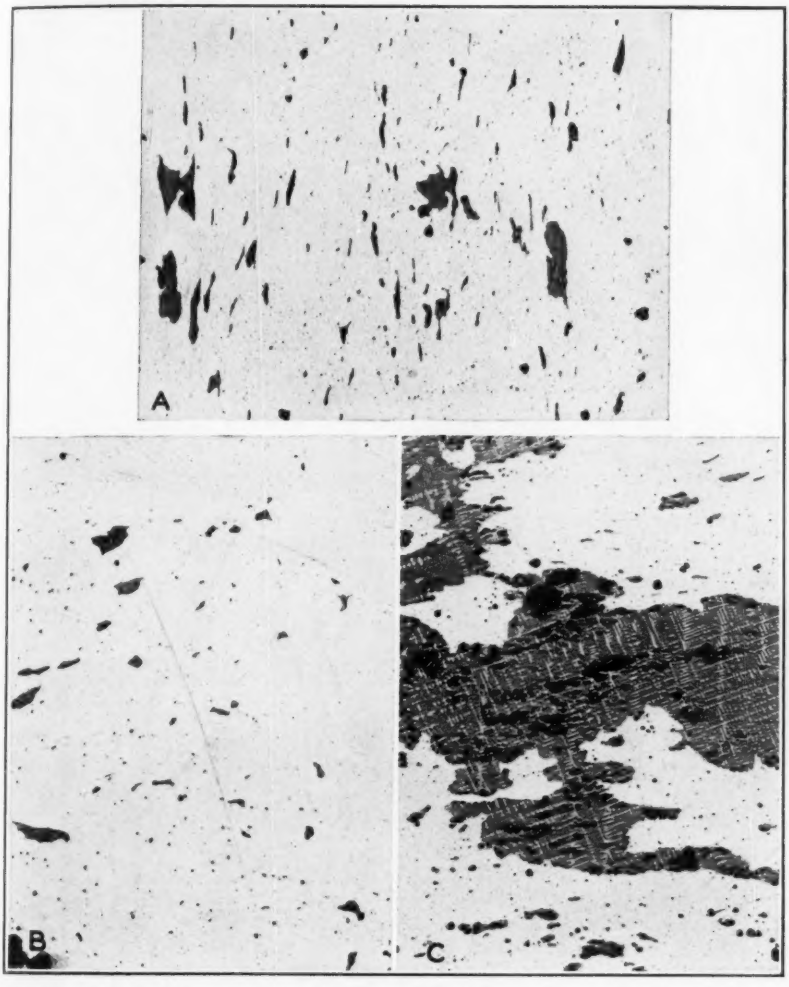

FIGURE 24.—*Microstructure of hand-puddled wrought iron in the muck-bar state, × 100, reduced to × 75*

The micrographs are of transverse sections, unetched. *a*, Area representing the average size of slag threads (transverse sections) and their distribution; *b*, shows an area with the slag threads as small as were found; and *c*, transverse section of a large slag thread. Such threads were not uncommon.

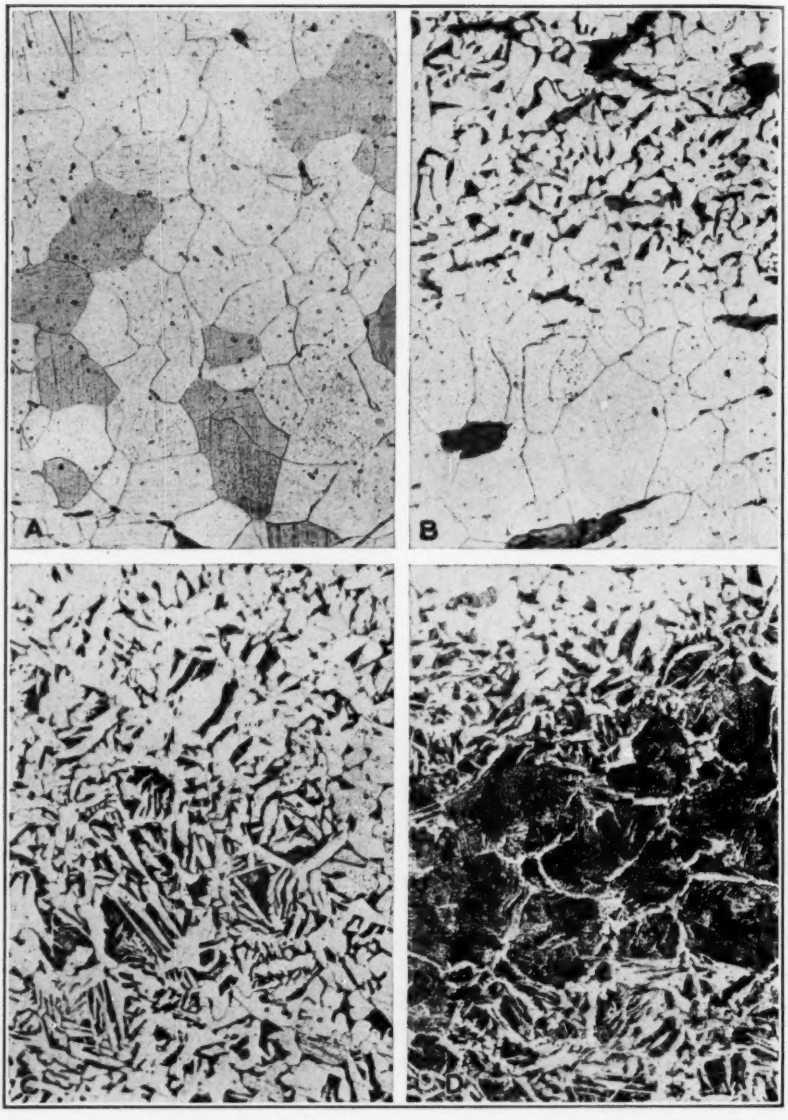

FIGURE 25.—*Microstructure of hand-puddled wrought iron in the muck-bar stage, × 100, reduced to × 75*

The specimens (transverse sections) were etched with an alcoholic solution of picric acid. *a*, A large part of the material showed no carbon, as is represented here; and *b*, *c*, and *d*, "carbon streaks" of increasing carbon content found scattered throughout the muck bar.

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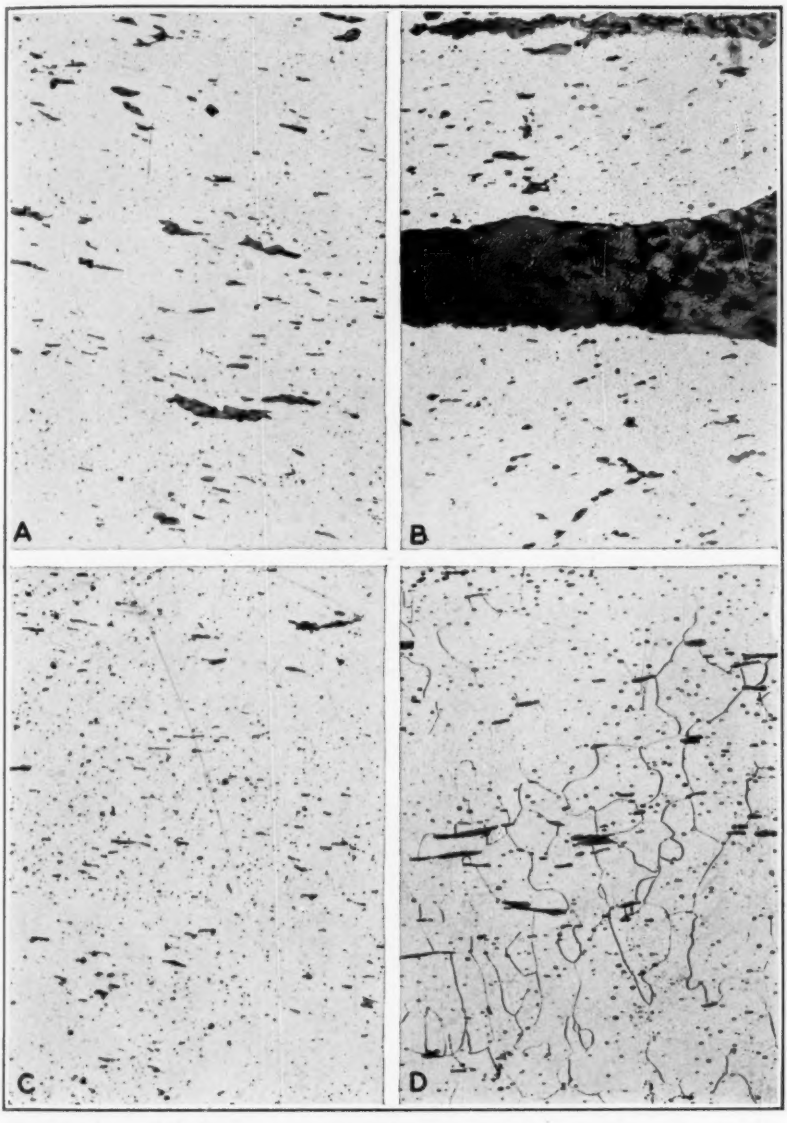

FIGURE 26.—*Microstructure of wrought iron made by the new process, in the muck-bar state, × 100, reduced to × 75*

The micrographs show transverse sections, unetched, except in *d*, which was etched with alcoholic picric acid solution. *a*, Area representing the average size and distribution of slag threads; *b*, area showing some of the largest slag threads found; *c*, area showing small slag threads; and *d*, appearance after etching. No carbon was found.

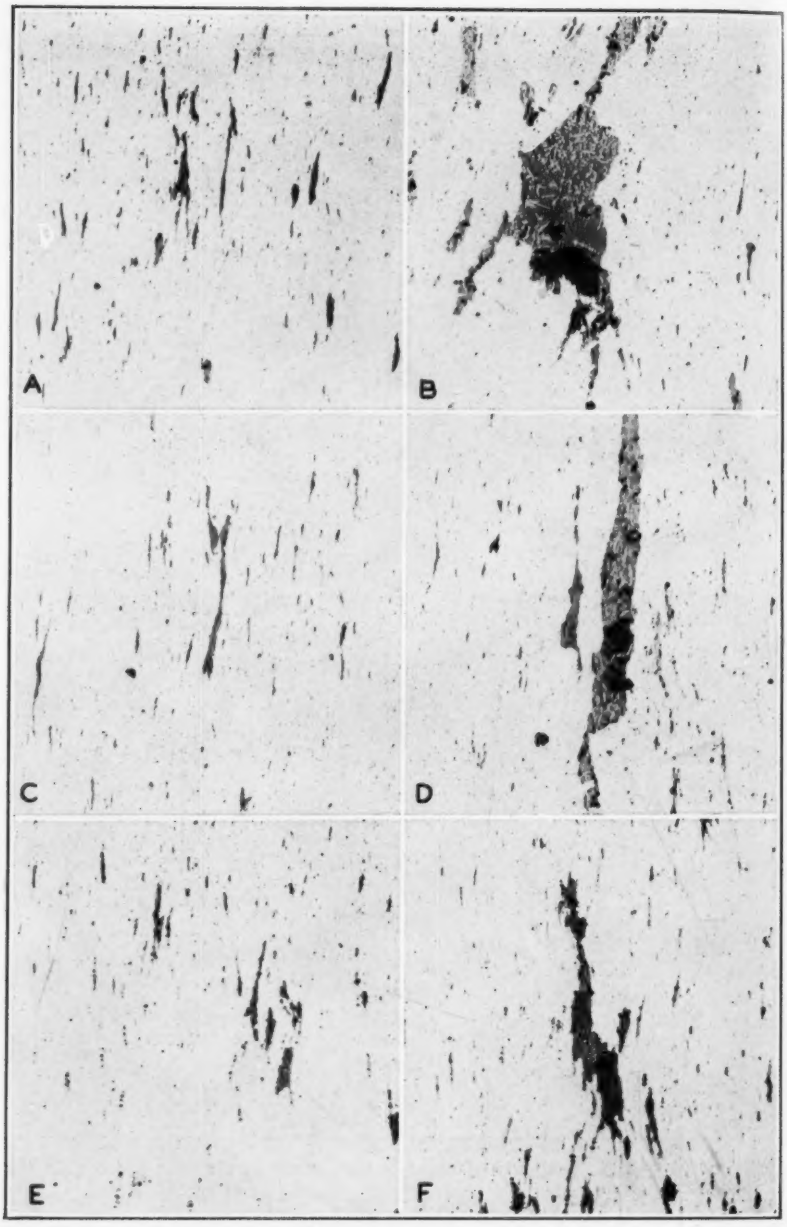

FIGURE 27.—*Microstructure of wrought iron in the form of pipe skelp, × 100, reduced to × 75*

The micrographs are of unetched transverse sections and represent the average condition of the slag (left) and some of the large slag threads (right). *a, b,* Hand-puddled iron; *c, d,* new process; and *e, f,* composite iron.

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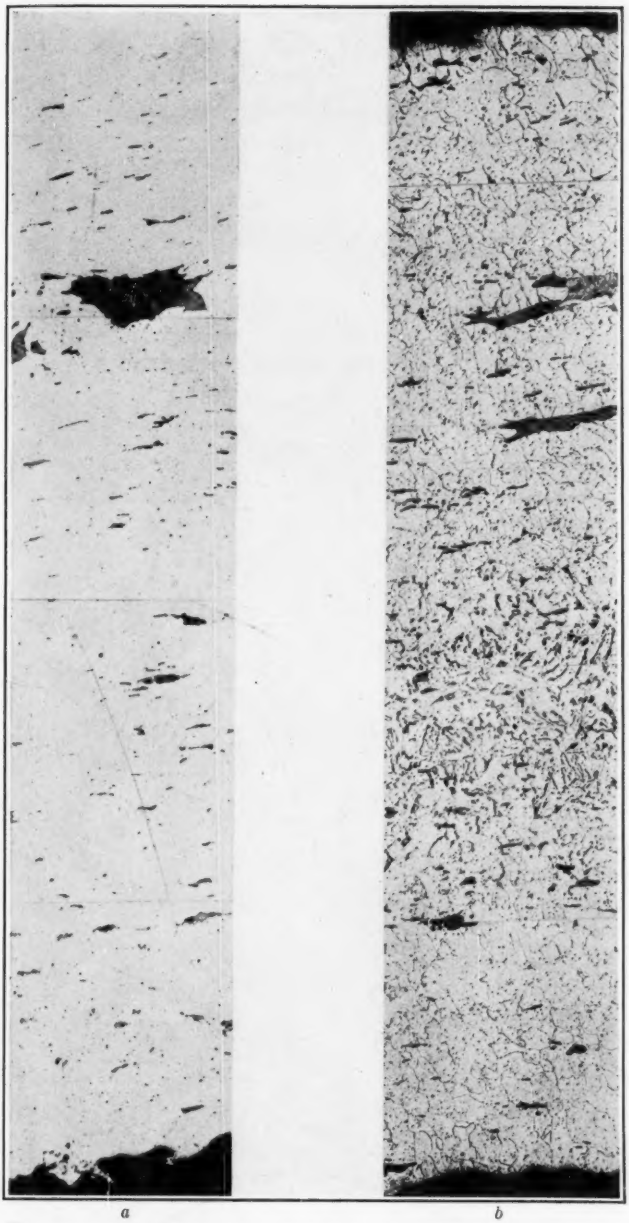

a *b*

FIGURE 28.—*Microstructure of hand-puddled wrought-iron pipe, × 100, reduced to × 50*

Transverse sections of the entire wall of two 1-inch pipes are shown. *a*, Unetched; *b*, etched with alcoholic picric-acid solution. Note the pearlite (carbon) in *b*.

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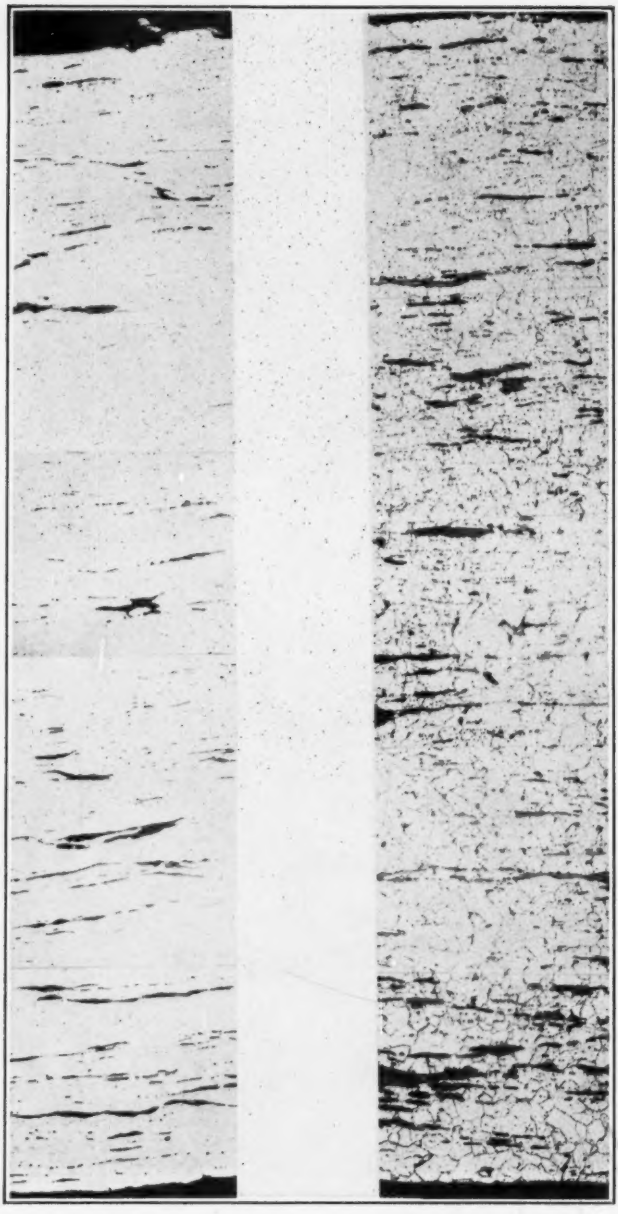

FIGURE 29.—*Microstructure of hand-puddled wrought-iron pipe,* $\times$ *50*

Longitudinal sections, unetched and etched, of the entire wall of a 1-inch pipe.

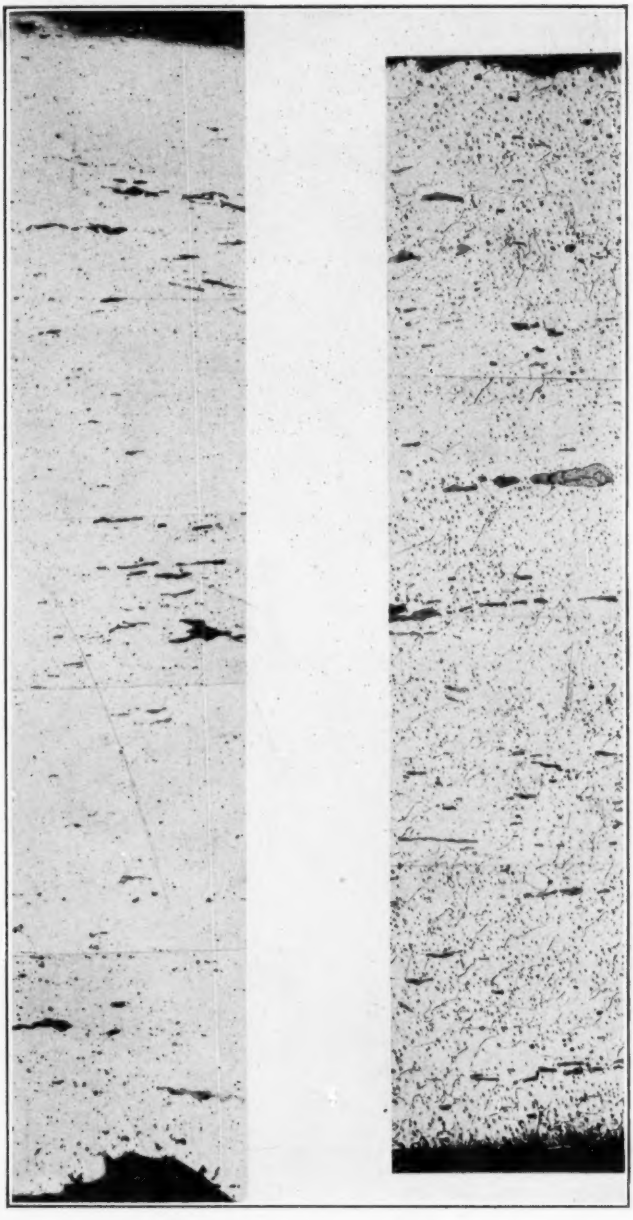

FIGURE 30.—*Microstructure of wrought-iron pipe made by the Aston process, × 100, reduced to × 50*

Transverse sections, unetched and etched, of the entire wall of two 1-inch pipes.

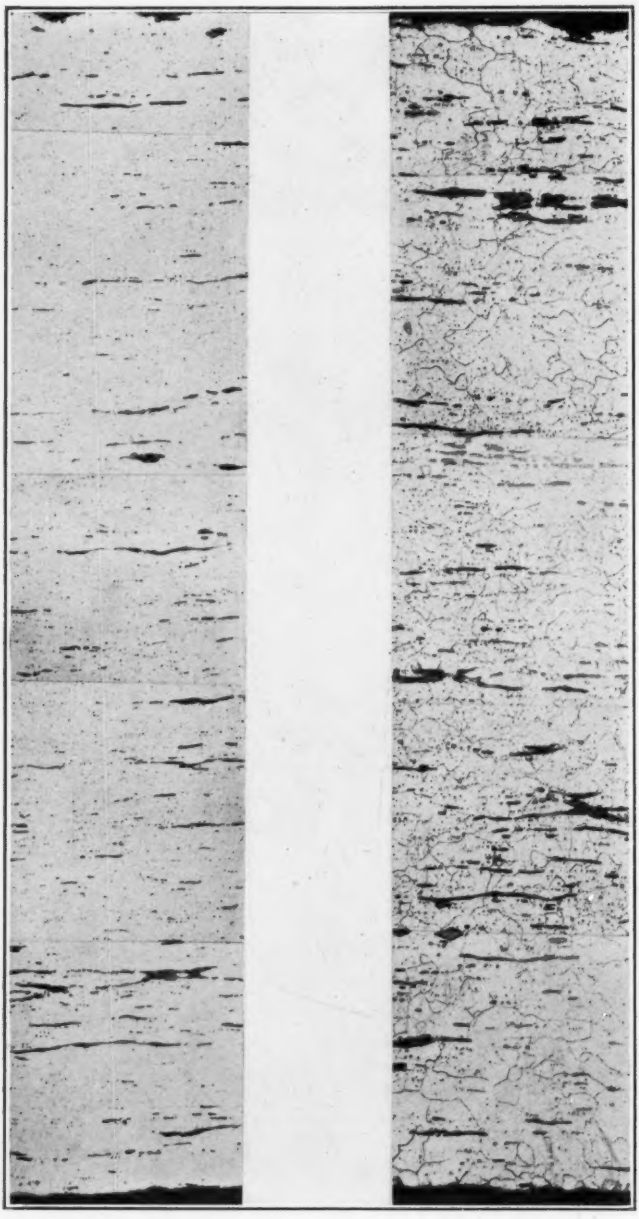

FIGURE 31.—*Microstructure of wrought-iron pipe made by the Aston process, × 100, reduced to × 50*

Longitudinal sections, unetched and etched, of the wall of a 1-inch pipe.

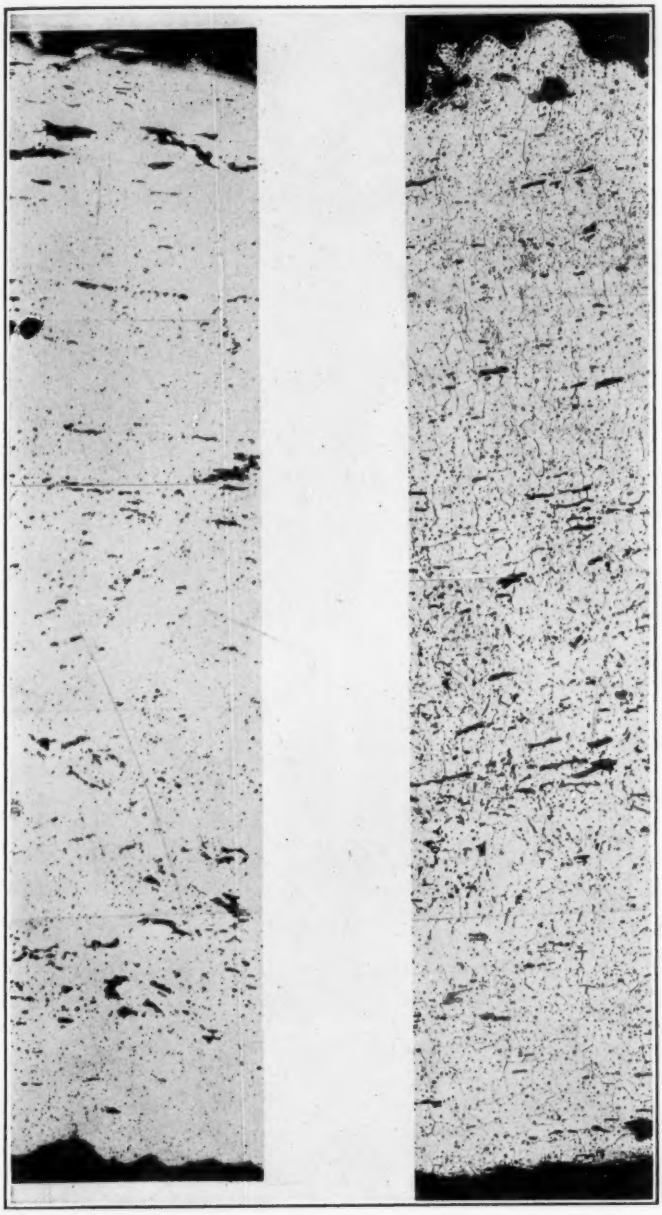

FIGURE 32.—*Microstructure of wrought-iron pipe, × 100, reduced to × 50*

Transverse sections, unetched and etched, of the wall of a 1-inch pipe made of the composite iron containing equal parts of hand-puddled and the new-process iron.

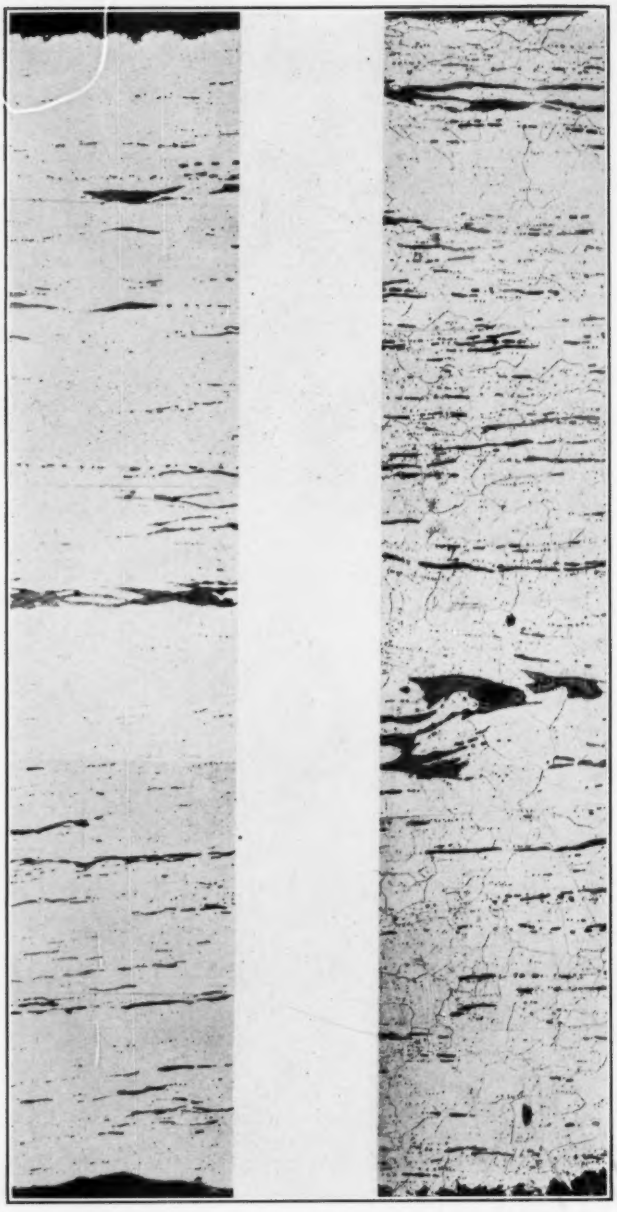

FIGURE 33.—*Microstructure of wrought-iron pipe, × 100, reduced to × 50*

Longitudinal sections, unetched and etched, of the entire wall of two pipes of the composite iron (equal parts of the two types of iron)

(3) SKELP.—The examination of samples of the skelp taken from the front, middle, and back of the strip as rolled showed no important differences in the structure corresponding to these three positions. The average distribution of the slag threads, together with some of the largest slag threads found, as seen in the transverse sections of each of the three kinds of skelp, is shown in Figure 27. The examination of this material after etching showed considerably more uniformity with respect to carbon distribution in the hand-puddled product than was found in the muck bar and ball stages. This is a natural consequence of the heating which the piles formed from the sheared muck bar received, together with the rolling into skelp. The average carbon content of the streaks which were found was estimated from the microstructure to be 0.15 to 0.20 per cent. A few of these streaks were found in the skelp rolled from the composite pile containing equal parts of the two types of iron.

(4) PIPE.—The structural condition of the iron after being worked into the form of pipe is depicted in Figures 28 to 33, inclusive. Transverse and longitudinal sections of the entire wall of the pipe are shown for each of the three kinds. There were no features found in any case which are not common in commercial wrought-iron pipe. The relatively cleaner appearance of the pipe made from the new iron and particularly the absence of "carbon streaks" is noteworthy. No very marked difference in the slag distribution in any of the three irons was noted, although the occurrence of relatively large slag threads in the hand-puddled iron was somewhat more frequent than in the comparison material.

(b) 1-INCH ROUNDS

The macrostructure of the wrought iron produced by the Aston process after being rolled into the form of 1-inch rounds is shown in Figure 34. The effect of the repeated piling or refining which some of this material received is very evident. No unusual features in the microstructure of the iron were noted. The size of the slag threads naturally varied somewhat with the amount of piling and rolling which the iron received. So far as can be judged from the microstructure alone, as is shown in Figure 35, this material would be considered as high-grade wrought iron.

(c) SLAG

Wrought-iron slag is essentially a ferrous silicate slag. According to Herty and Fitterer,[9] such slags containing silica in amounts less than 29 per cent contain two constituents, FeO and a silicate, fayalite ($2FeO\text{-}SiO_2$). The eutectic for this part of the system occurs

[9] C. H. Herty and G. R. Fitterer, The Physical Chemistry of Steel Making: Deoxidation with Silicon and the Formation of Ferrous-Silicate Inclusions in Steel, Bull. 36, Min. & Met. Investigations, Carnegie Institute of Technology and Bureau of Mines; 1928.

with a silica content close to 21 per cent. Pure ferrous silicate slags containing less than 21 per cent silica, therefore, consist of excess FeO embedded in a eutectic matrix of FeO and fayalite. This is the structural condition which obtains in wrought-iron slags ordinarily. The eutectic is extremely fine and appears as a single constituent at the magnifications ordinarily used in studying the structure of wrought iron.

It will be noted (fig. 36) that slags representative of the product of hand puddling and of that of the new process have the same general structure and show no essential differences in structure such as would be considered significant of marked differences in properties. These samples, which were secured as drippings from the wrought-iron ball, were remelted in the laboratory in iron crucibles and allowed to cool slowly in the furnace so as to approach a condition of equilibrium.

Observations were made on the behavior of the two slags when heated to fusion, the samples being contained in small iron crucibles and heated in an Arsem vacuum furnace, the pressure within the furnace being somewhat less than that equivalent to 1 mm of mercury. Both slags melted quietly in the crucibles and there was no evidence of any loss by sputtering. A crucible containing hand-puddled slag, which had been previously ground in a mortar, weighing 17.5 g (crucible 6.8 g) weighed 17.3 g after heating. Similar weights for the slag of the new process were 17.9 g before heating (crucible, 6.9 g) and 17.8 g after fusion of the slag.

Observations by means of an optical pyrometer of the "disappearing filament" type, of samples heated similarly to these showed that the new-process slag gave distinct visible evidence of melting at 1,280° C. (2,335° F.) and was completely molten at 1,350° C. (2,460° F.). Upon slowly cooling, this slag appeared completely frozen at 1,270° C. (2,320° F.). Slag from the hand-puddling process showed evidence of melting at 1,250° C. (2,280° F.) and was completely liquid qt 1,350° C. (2,460° F.). On cooling, it had the appearance of being completely frozen at 1,220° C. (2,230° F.).

Figure 37 shows the appearance of the surface of the two samples after being melted and allowed to freeze in the crucible. It will be noted that the slag from the hand-puddled process shows numerous shrinkage holes or "pores" over the surface which may be related to the evolution of gases during freezing. These were lacking in the comparison sample which froze with a continuous though slightly roughened surface.

A series of determinations of the relative viscosity of the two slags was made [10] in the plant, the slag in each case being taken directly

[10] These determinations were made by members of the staff of the Bureau of Mines, Pittsburgh station.

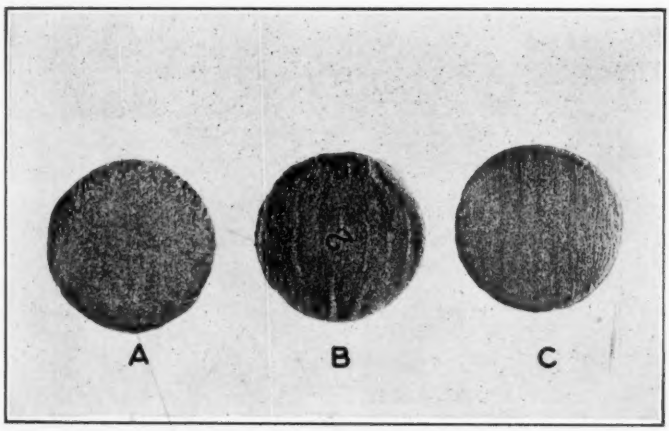

FIGURE 34.—*Microstructure of the new-process wrought iron in 1-inch rounds,* $\times$ $\frac{3}{4}$

a, "Direct rolled"; *b*, "single refined"; *c*, "double refined." Etchant, 4 per cent nitric-acid solution.

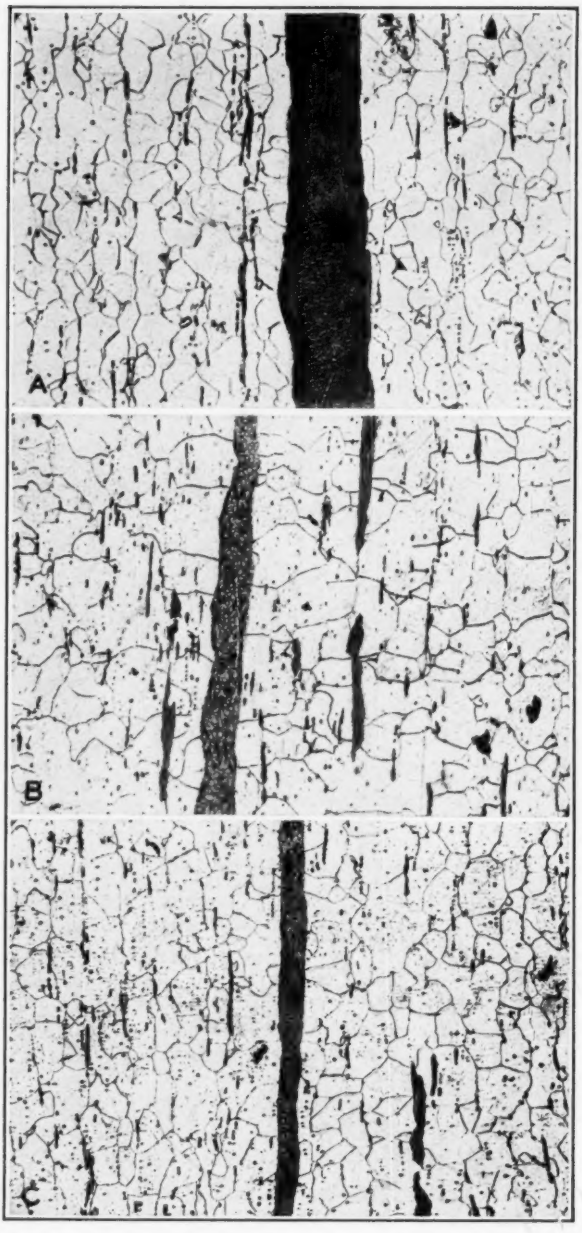

FIGURE 35.—*Microstructure of the new-process wrought iron in 1-inch rounds, × 100, reduced to × 75*

a, "Direct rolled" iron; *b*, "single refined" iron; *c*, "double refined," iron. The large slag threads illustrate the relative size of such threads in the three grades of iron. Such threads are only occasionally found. Etchant, alcoholic picric-acid solution.

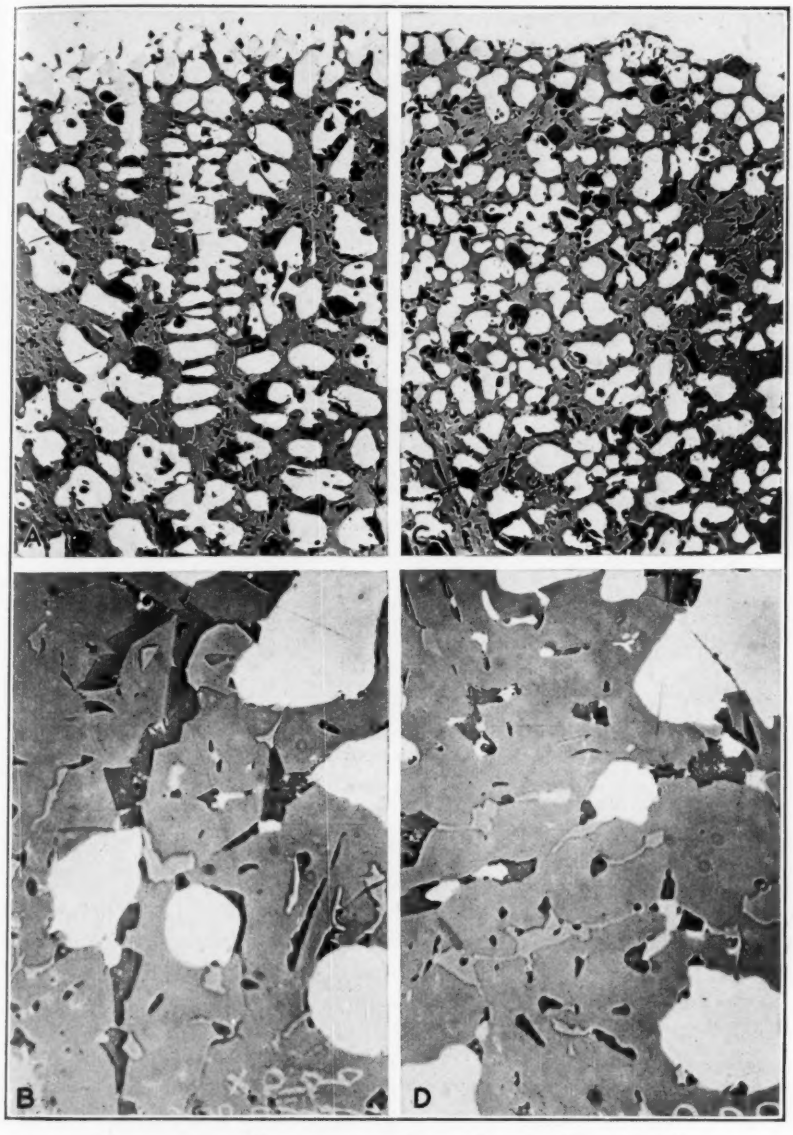

FIGURE 36.—*Microstructure of wrought-iron slag, unetched*

The slags obtained as drippings from the "ball" were melted in iron crucibles in a vacuum furnace and allowed to cool slowly. In both slags, the light areas are FeO; the gray background is fayalite. Note, in *b* and *d*, the other structural constituents embedded in the fayalite matrix. *a*, Slag from hand-puddled iron. The light portion at the top of the micrograph represents the iron crucible. Note how the slag has penetrated into it, × 100, reduced to × 75; *b*, Same as *a*, × 500 reduced to × 375; *c*, slag from the new-process iron, × 100 reduced to × 75; *d*, same as *c*, × 500, reduced to × 375.

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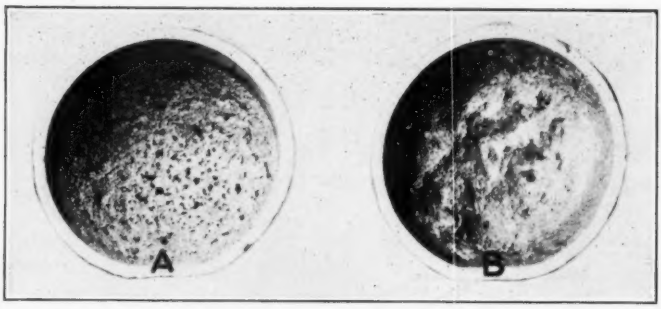

FIGURE 37.—*Surface appearance of wrought-iron slags after remelting followed by slow cooling,* × 2

The photographs show the surface of the slag after being melted and allowed to solidify in the crucible. *a*, Slag from hand-puddled iron; *b*, slag from new-process iron.

either from the puddling furnace or from the "shotting" cup, for the new process. The inclined-plane method was used. The plane forms an angle of 30° with the horizontal and the thickness of the layer formed as the molten slag flows down the plane was measured at a distance of 12 inches from the top of the plane. The results are summarized in Table 17. It will be noted that according to these results, the slag taken from the hand-puddling furnace was somewhat more viscous than that of the new process.

TABLE 17.—*Relative viscosity of slag of the hand-puddling process and of the new process*

[The inclined plane method was used. The thickness of the slag layer was measured 12 inches from top of the plane]

Material	Sample No.	Condition of sampling	Temperature [1]		Thickness of slag layer
			° *F.*	° *C.*	*Inch*
Hand-puddled slag	H1	During the boil	2,400	1,315	0.075
	H2	do	2,400	1,315	.077
	H3	do	2,400	1,315	.080
	H4	do	2,400	1,315	.085
	H5	Slag remaining in furnace after removal of ball	2,520	1,380	.072
	H6	do	2,520	1,380	.070
	H7	do	2,520	1,380	.075
New-process slag	A1	From slag thimble before shotting	2,400	1,315	.045
	A2	do	2,400	1,315	.044
	A3	do	2,400	1,315	.052
	A4	do	2,400	1,315	.065
	A5	do	2,350	1,290	.072
	A6	From slag thimble after shotting	2,400	1,315	.042
	A7	do	2,400	1,315	.043
	A8	do	2,400	1,315	.057
	A9		2,400	1,315	.051
	A10		2,400	1,315	.042

[1] Temperatures are only approximate.

Wrought-iron slags always contain other substances besides FeO and SiO_2. (Table 4.) A considerable amount of the iron may be in the ferric condition (Fe_2O_3) and phosphorus is always present as well as some other constituents. Evidence of other structural constituents in addition to FeO and fayalite can practically always be found in such slags. (Fig. 36.) No difference in the two slags were noted in this respect.

6. MISCELLANEOUS TESTS AND OBSERVATIONS

(a) OBSERVATIONS ON BLISTERING

It is well known that "blisters" are quite common on the inner surface of wrought-iron pipe of the smaller sizes. In cutting up the pipe lengths used in this study which had been chosen at random without any inspection, whatsoever, a few blistered areas were noted and in such cases that portion of the pipe was not used for test specimens. It is of interest to note that such blisters were confined almost entirely to the pipe made from the hand-puddled iron. Undoubtedly

the formation of these blisters is associated with the occasional "carbon streaks" which occur in this type of iron and is to be attributed to the liberation of gas (CO) in the reaction between the combined carbon and the ferrous oxide of the slag. The fact that the iron made by the new process has a very low carbon content, (rarely over 0.03 per cent), in all stages of fabrication, from the ball to the finished pipe, is believed to account for the relatively high degree of freedom of this type of pipe from this feature. Figure 38 shows the appearance of some of the blistered areas.

(b) BEHAVIOR ON CARBURIZING

It has been demonstrated beyond all reasonable doubt [11] that, by means of carburizing such as is done in the common casehardening process, certain differences in steel can be shown which are detectable in practically no other manner. It appeared of interest, therefore, to apply this test, which is ordinarily referred to as the "McQuaid-Ehntest," to the two types of iron. Samples of the muck bar and skelp of both the hand-puddled iron and the comparison iron made by the new process were carburized by being heated for eight hours at 940° C (1,725° F.), while embedded in a commercial carburizing compound and then being allowed to cool in the furnace. The microscopical examination [12] revealed no essential difference in the structure of the carburized irons. Both irons showed a very "abnormal" structure, the term being used in the same sense as it is applied to carburizing steels.

(c) MILL OBSERVATIONS

"Weldability" and ease of machining rank high among the desirable characteristics of wrought iron. Observations on the relative weldability of the two types of iron as it was being made into pipe were made in the mill, together with the usual flattening and hydrostatic tests which form part of the routine mill tests. The new-process iron behaved in all essential respects in these tests like the hand-puddled iron. Such visual observations as it was possible to make on the machining of the pipe in the mill indicated no difference in the behavior of the two irons during the threading of the ends of the pipe. Likewise the observations made on the behavior of the two during galvanizing, supplemented by flattening tests of the galvanized pipe, indicated that the "galvanizing properties" of the new iron are equal in all respects to those of the hand-puddled product.

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[11] S. Epstein and H. S. Rawdon, Steel for Case Hardening—Normal and Abnormal Steel, Bureau of Standards Journal of Research, **1**, 423, 1928; Research Paper No. 14.

[12] This test was carried out by Samuel Epstein, associate metallurgist.

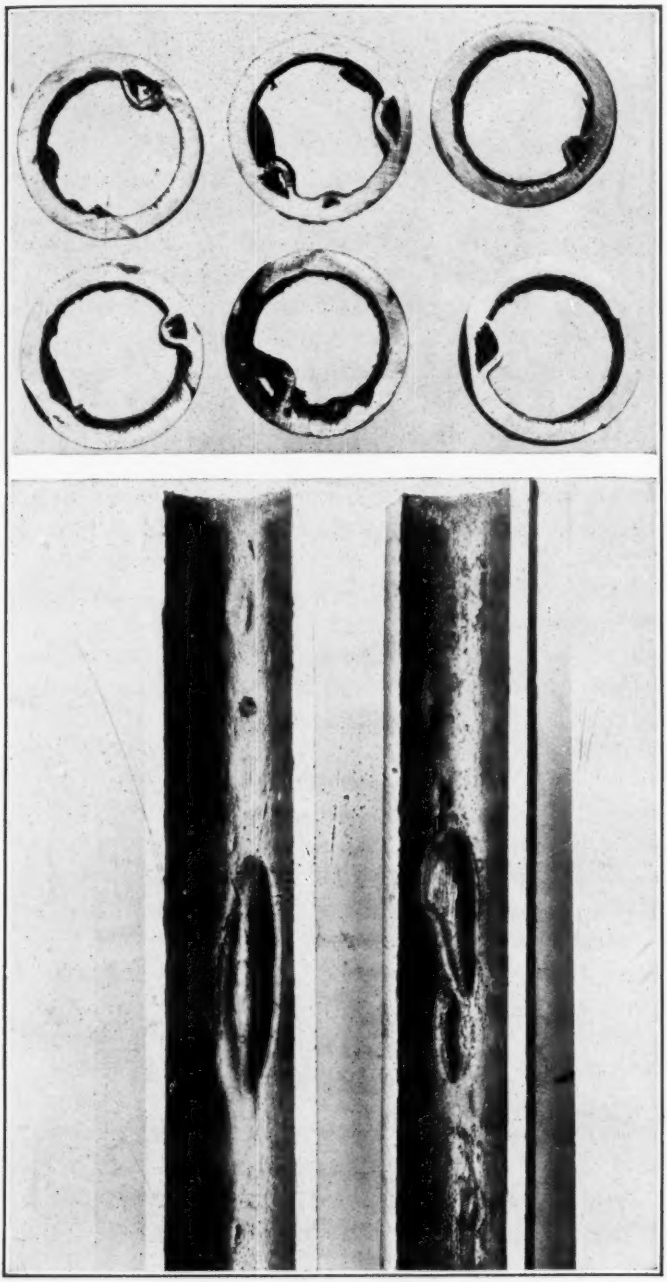

FIGURE 38.—*"Blisters" in wrought-iron pipe*

The transverse and longitudinal sections show the blistered appearance of the inner pipe surface which is frequently observed.

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V. DISCUSSION

Wrought iron is universally conceded to be a malleable product formed from the refining of pig iron (or ore) by the almost complete elimination of the metalloids in the material and, in the wrought state, has a characteristic structure referred to as "fibrous," which is the result of the intimate mechanical mixture of some slag with the iron. Since wrought iron is a mixture of two unlike substances, its composition, at least as determined by ordinary chemical analysis can not readily be used as a basis of a definition as may be done in the case of steel. The refining of the raw material must necessarily be quite complete in order to obtain a malleable product. The metalloids initially present in the pig iron, if not entirely eliminated, are reduced to a very small percentage. Aside from the restriction concerning the maximum percentage of manganese permitted, for example, 0.10 per cent,[13] chemical composition is not usually specifically mentioned in specifications for wrought iron. In the results of the chemical analyses of the different irons summarized in Table 3, nothing will be found which could be used as a basis of adverse criticism of any of the irons. It will be noted that the carbon content of the new-process iron was lower than that of the comparison iron, and, as shown by the metallographic examination, this product showed no nonuniformity such as would result from "carbon streaks." It should not be inferred, however, that nonuniformity by the presence of carbon streaks is necessarily a characteristic of all wrought iron made by the hand-puddling process.

On the basis of the density measurements, there is little to be said concerning the possible differences in the two types of iron. As might be predicted, the iron in the form of muck bar was somewhat less dense than after being rolled into skelp or pipe, the hand-puddled muck bar showing a slightly lower density than the comparison iron. This was also true in the case of the pipe and skelp, the differences were so slight, however, as to appear to be of no practical significance.

For purposes of comparison, the average tensile properties of the pipe materials have been summarized in Figure 39. The properties of the iron in the form of muck bar, are of course, of no practical concern; the fact is of some interest, however, that iron made by the new process even in this rough form, showed considerably higher ductility, though with a somewhat lower tensile strength, than the hand-puddled iron did. The presence of combined carbon in the latter in sufficient amounts as to form easily recognized "carbon streaks" is probably the reason for this difference. The working

[13] Specifications A84-27 and A86-27, Am. Soc. Test. Mtls. Standards; 1927.

which the materials received in putting them into the form of skelp and pipe improved the tensile properties. It will be noted, however, that, in general, the hand-puddled iron after the additional rolling

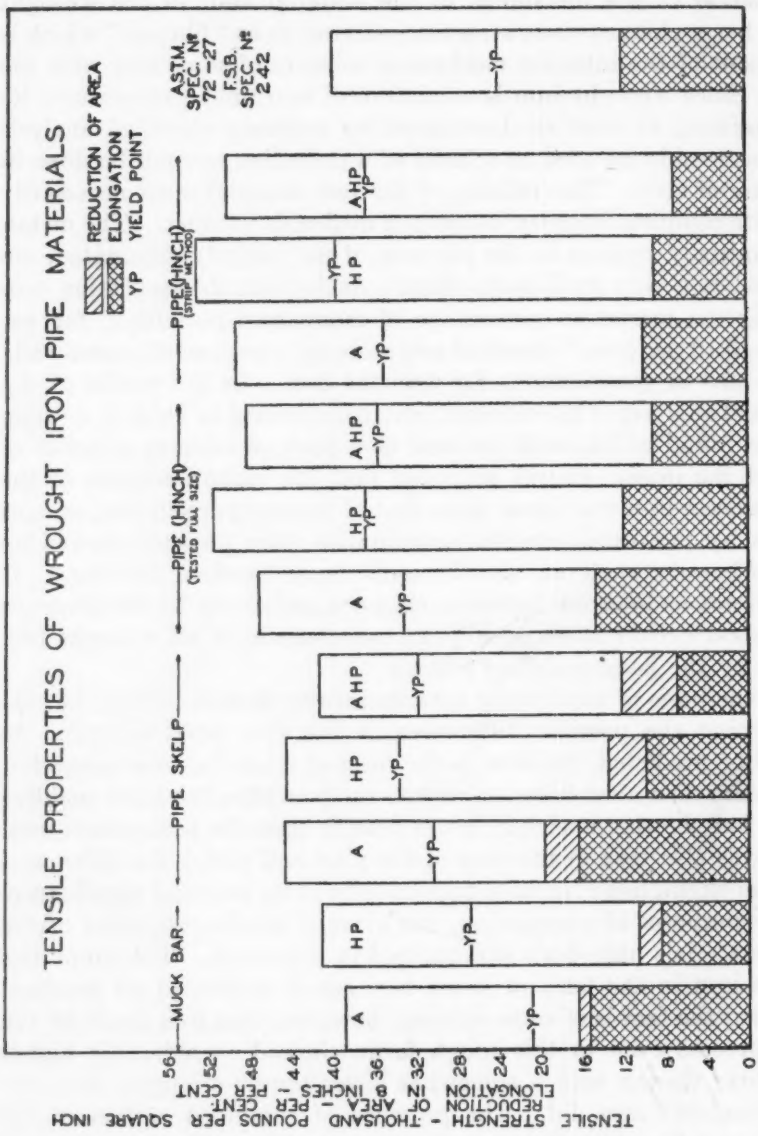

FIGURE 39.—*Comparison of the tensile properties of wrought-iron pipe with specification values*

A=new-process iron, *HP*=hand-puddled iron, *AHP*=the composite iron containing equal parts of *A* and *HP*

still showed considerably higher tensile strength, accompanied by lower ductility, than did the comparison wrought iron.

By comparison with the tensile properties for wrought-iron pipe of this size as required by specifications of the American Society for

Testing Materials and the Federal Specifications Board,[14] it will be seen that both the hand-puddled wrought iron and the new process wrought iron when tested as full-size specimens, would meet the required tensile properties. However, when the tensile properties were determined on longitudinal strips machined from the pipe, as is permitted by current specifications, the average elongation was found to be lowered very considerably. This lowering of the elongation is to be attributed to the form of the test specimen and not to any inherent property of the iron. The specimen, in each case, represented the full wall thickness and the intitial curvature was maintained through the test. On the bases of these tests, it would appear that in testing pipe of small diameter, the strip method, at least as carried out here, is not suitable and should not be depended upon.[15]

The torsional properties of wrought iron are not ordinarily taken into account in specifications for pipe. For rotary drill pipe, of course, the behavior of the pipe under torsion may be of considerable importance. The torsion tests, in the present study, however, afforded another convenient means for comparing the properties of the two irons, in the form of pipe. It will be noted (Table 10) that the results of the torsional tests confirmed those of the tension tests in showing that the hand-puddled iron used was a slightly stronger, but somewhat less ductile material than the comparison wrought iron.

The properties of the new iron when rolled into the form of 1-inch rounds compare favorably with those of high-grade hand-puddled wrought iron made commercially in this form. The tensile properties and impact resistance are summarized in Figure 40, together with the corresponding properties of 1-inch rounds of high-grade wrought iron which were obtained in a previous series of tests.[16] It has already been stated that the 1-inch rounds used in the present study were especially rolled for these tests under regular mill conditions. The comparison materials represent wrought-iron rounds made to meet certain specifications of the American Society for Testing Materials.

It is evident from the results of nearly all of the tests carried out upon the 1-inch rounds of the new-process iron (Tables 12, 13, 14, and 15) that the amount of working, that is, refining (piling and reheating) which the iron received did not affect its properties to a very marked extent. The tensile, torsional, and "single-blow notched-bar" impact resistance properties were found not to differ

[14] Standard specifications A72-27, Am. Soc. Test. Mtls. Standards, 1927. Also Federal Specifications Board, specification 242, "Wrought Iron Pipe, Welded (Black and Galvanized); 1925.

[15] Specification 242 of the Federal Specifications Board is now being amended in this respect, the question having been brought up for consideration by another manufacturer of wrought-iron pipe. For the determination of the tensile properties of pipe 2 inches in diameter and less, the tension specimens consist of full-size pipe sections, the strip method being restricted to the pipe of larger diameter.

[16] See footnote 4, p. 954.

greatly for the "direct-rolled," the "single-refined," and the "double-refined" irons. To supplement the impact tests (single-blow notched-

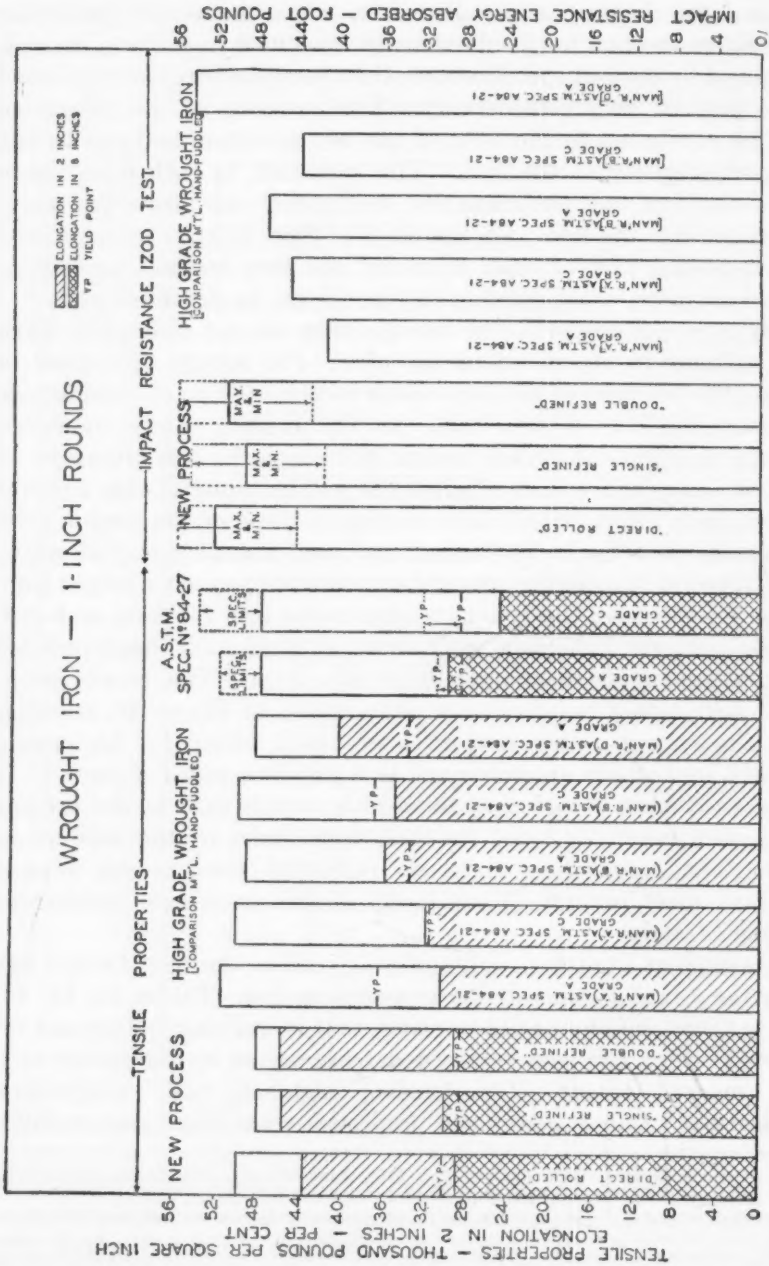

FIGURE 40.—*Comparative properties of wrought iron 1-inch round*

bar), the ends of the specimens were etched, after the test, to show the macrostructure in order to find out how the blows had been struck

with respect to the piling. In the majority of cases, the maximum resistance was shown when the blow was struck against the face of the "slabs." However, it was noticed that, when the three blows for any one specimen were struck at 45° to the face of the slabs, as was the case for a number of specimens, the difference between the maximum and minimum was as great, in some instances, as when the blows struck the face and edge of the slabs. It would appear, however, from the results obtained in the repeated-blow impact tests (Table 15) that the impact resistance of the iron against repeated blows was noticeably improved by the additional "refining" which was given the iron.

In carrying out the corrosion tests no attention whatsoever was given to the controversial question as to the relative corrodibility of wrought iron and steel. The sole purpose of the tests was to show whether or not the corrosion behavior of the two types of iron, in the form of pipe, differed to any marked extent. A comparison of the results for the wrought iron made by the Aston process with those for the hand-puddled product indicates a very slightly higher corrosion resistance for the latter. These indications are in accord with the results of the tests carried out to show the relative electrolytic solution potential of the two. These tests indicated that the new-process iron, when in electrical contact with the hand-puddled iron, both being immersed in a solution, behaves as the anode of the couple; that is, it has a higher solution pressure. It might be argued therefore, that it might be unwise to use the two different kinds together. The results obtained with the pipe made from the composite iron, which was rolled from an 8-high pipe of muck bar composed of equal amounts of the two types of iron did not confirm this prediction.

As might be expected, the method of the corrosion test had a marked influence on the apparent corrosion resistance of the irons. The average sorrosion loss obtained in simple immersion in tap water or in 3½ per cent sea-salt solution (unaerated) was in the neighborhood of 0.006 to 0.007 g/dm²/day, whereas the loss for the same irons in the same solutions, when aerated for 8 hours of every 24, was approximately four to five times as great (0.021 to 0.034 g/dm²/day). In the wet-and-dry corrosion tests, the loss was much more pronounced (0.125 to 0.168 and 0.05 to 0.07 g/dm²/day in sea-salt solution and tap water, respectively). It is evident that the effect, on the corrosion behavior of these materials, of the conditions under which the corrosive attack was brought about far overshadowed possible effects resulting from differences in the materials.

Of the different corrosion methods used, the immersion tests, without question, are more nearly representative of conditions for pipes in service than the wet-and-dry tests are. And of the two types of immersion tests, those carried out in tap water which was not exces-

sively aerated probably represent service conditions for the large majority of pipe better than the other immersion tests. It is evident from Figure 15, that on the basis of the results obtained with the simple immersion tests in either of the liquids used, no sharp distinction as to the relative merits of the various materials can be drawn. Likewise, the average corrosion losses obtained in the immersion tests in highly aerated liquids, especially those in tap water, do not differ sufficiently to warrant sharp distinctions being drawn as to the relative corrosion resistance of three materials.

Concerning the similarity in structure of the two types of iron, little need be said. The micrographs clearly show that the product made by the new process has the structural features which are generally considered to be characteristic of wrought iron. Indeed, it is extremely doubtful whether any metal microscopist could distinguish with certainty a sample of the new wrought iron from iron made by the familiar hand-puddling process if the sample were submitted to him as an "unknown." The almost complete absence of carbon streaks from the structure of the iron made by the new process is a noteworthy feature and any possible distinction between the two irons from the standpoint of structure would undoubtedly have to be drawn on this basis.

The examination of the slag from the two different processes showed that both were essentially ferrous silicate slags containing an excess of iron oxide, although not absolutely identical in either chemical composition or structure. The slight differences, however, would not seem to be of importance from a practical standpoint so far as the properties and use of the finished product are concerned.

In the observations made in the mill, especially on the welding, galvanizing, and machining properties of the two types of iron in the form of pipe, nothing was seen to indicate any marked differences in the two irons in these respects.

VI. SUMMARY

1. A comparison was made of the properties and structure of wrought iron made by the hand-puddling process with those of wrought iron produced by a new process. The new process differs radically from the conventional hand-puddling process in that the pig iron after being melted in a cupola is refined in a Bessemer converter and then incorporated with the slag which has been prepared in a separate furnace. The "shotting" operation by which the slag is intimately mixed with the iron consists in pouring the molten metal into a bath of the molten slag. The resulting "ball" after being squeezed into a bloom is rolled in the ordinary manner into the desired shape. The comparison tests were carried out largely upon commercial 1-inch butt-welded black pipe, since, as yet, the commer-

cial use of the new process is confined almost entirely to pipe. Three types of pipe were used, hand-puddled iron, new-process iron, and a "composite" iron composed of equal parts of the other two. Tests were also made upon the muck bar and skelp from which the pipe was rolled. The samples were chosen at random in the mill, and each length was sampled so as to obtain samples representative of the front, middle, and back, as rolled, of the strips selected. All of the succeeding tests were made on all of these samples. In addition to pipe materials, tests were made upon the new-process wrought iron in the form of 1-inch rounds, rolled especially for this work.

2. The chemical composition of the iron made by the new process was found to agree closely with that of the hand-puddled iron. The carbon content was consistently lower in the new-process iron than in the comparison iron and more uniform in that "carbon streaks" were entirely absent in the structure as shown by metallographic examination. The sulphur content of the new-process iron was not quite so low as that of the hand-puddled product.

3. No marked differences in density were found in the irons. The new-process iron had a slightly higher density, but the difference was so slight as to appear to be of no practical significance.

4. No marked difference in mechanical properties were found in the two irons, in pipe form, as shown by tension, torsion, and flattening tests. The iron made by the Aston process, on the whole, showed a slightly lower tensile strength accompanied by a higher ductility. Pipe made from the new-process iron meets the requirements of current specifications for pipe of the American Society for Testing Materials and the Federal Specifications Board.

5. In the form of 1-inch rounds the wrought iron made by the new process was found to compare very favorably in mechanical properties with standard grades of wrought iron of this form. The properties studied included tensile and torsion properties and the resistance of notched bars to single-blow and repeated-blow impact. Except in the "notched-bar repeated-blow" impact resistance, no important differences were noted in the different amounts of "refining" which the rounds received. The material used was representative of "direct-rolled," "single-refined," and "double-refined" iron.

6. The accelerated laboratory corrosion tests indicated very slight differences in the corrosion resistance in favor of the hand-puddled iron. These differences were extremely slight as compared with the differences in corrosion behavior resulting from the different test methods used.

7. The structural features of the iron made by the Aston process are those which are generally conceded to be characteristic of wrought iron in general. The absence of "carbon streaks" in the new-process iron is noteworthy. It is not to be concluded, however,

that this feature is necessarily always present in hand-puddled iron. The puddling process is not nearly so favorable for the complete elimination of carbon, however, as is the new process. The occurrence of occasional relatively large slag threads in the hand-puddled iron was more frequent than in the comparison material according to the examination made.

8. Although not a primary object of this investigation, general observations made of the hand-puddling process and of the Aston process seemed to indicate a close parallelism in the important reactions entering into the manufacture of wrought iron in the two cases. The similarity of the products of the two processes confirm this indication.

9. In the observations made in the mill nothing was observed that would indicate that the behavior of the new-process wrought iron in welding, galvanizing, and machining is different from that of the wrought iron with which it was compared.

In addition to the acknowledgments made throughout the text, the authors wish to express their indebtedness to C. E. Eggenschwiler, junior laboratory assistant, for his very efficient help in a great many of the tests reported.

WASHINGTON, July 2, 1929.

A GRAVIMETRIC METHOD FOR THE DETERMINATION OF RUTHENIUM

By Raleigh Gilchrist

ABSTRACT

A gravimetric procedure for the accurate determination of ruthenium by hydrolytic precipitation from chloride solution has been developed. A delicate test for the qualitative detection of small quantities of ruthenium, using thiourea as a reagent, is described.

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I. INTRODUCTION

In the analysis of a material containing the platinum metals, such as crude platinum, osmiridium, etc., it has been the customary procedure, since the work of Deville and Stas,[1] to separate ruthenium by distillation with chlorine from an alkaline hypochlorite solution. The ruthenium tetroxide set free is absorbed either in a solution of hydrochloric acid containing some alcohol, or in a solution of an alkali hydroxide, likewise containing some alcohol.

Quite recently the separation of ruthenium by distillation with perchloric acid[2] has been proposed in a scheme of qualitative analysis. Although this separation is apparently very satisfactory

[1] H. Ste-C. Deville and J. S. Stas, Procès-verbaux, Comité International des poids et mesures, p. 194; 1877.

[2] Noyes and Bray, Qualitative Analysis for the Rare Elements. The MacMillan Co.; 1927.

for the purpose intended, a strictly quantitative study of it has not been made. This is true also of the separation by distillation with chlorine. Before a study of such separations could be made it was necessary to develop an accurate method for the quantitative recovery of ruthenium from solutions used as absorbents for ruthenium tetroxide. The experiments described in this paper were designed to develop such a method.

Of the methods previously proposed for the determination of ruthenium in the absorbent solutions none has been entirely satisfactory. Deville and Stas simply evaporated in a crucible the entire acid solution, containing the ruthenium as chloride, reduced the dried chloride thus obtained, washed the residue with water to remove any soluble salts, and weighed the ruthenium as metal. This procedure is somewhat troublesome at best and is clearly impracticable if large amounts of alkali halides are present.

Howe and Mercer [3] preferred to use a dilute solution of potassium hydroxide containing some alcohol as the reagent to absorb the ruthenium tetroxide separated by distillation. These authors precipitated the ruthenium as an oxide from this alkaline solution by gentle warming. They state that here the success of their work from the standpoint of quantitative determination ceased; that no satisfactory method could be found to collect this oxide for weighing, as it was impossible to free it from the alkali present. The oxide so obtained became colloidal after a single washing. They moistened the partially washed and dried precipitate with a few drops of hydrochloric acid, burned it, reduced the residue in hydrogen, washed the metal obtained with boiling water, and reduced again in hydrogen. The conclusion was that the method was too complicated for quantitative work.

Recently volumetric methods have been introduced, more particularly in the investigation of the constitution of the complex ruthenium salts, and especially with reference to the state of valency possessed by the ruthenium. A volumetric method in which iodine, liberated from potassium iodide through oxidation by ruthenium, is titrated with sodium thiosulphate has been employed by Krauss,[4] Krauss and Kükenthal,[5] Charronat,[6] Gall and Lehmann,[7] and others.

Howe,[8] failing to obtain satisfactory analytical results with potassium iodide, investigated a volumetric method using stannous chloride. Howe sums up his work on the titration with stannous chloride by saying that it should be noted that in almost every case the amount of stannous chloride required for reduction was somewhat lower than that called for by theory. For this reason, he says, the method can not be recommended for the accurate determination of ruthenium, but it does afford a ready method for the approximate evaluation of ruthenium solutions and for the determination of ruthenium when only a small amount is present.

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[3] Jas. L. Howe and F. N. Mercer, J. Am. Chem. Soc., **47**, p. 2926; 1925.
[4] F. Krauss, Z. anorg allgem. Chem., **117**, p. 111; 1921.
[5] F. Krauss and H. Kükenthal, Z. anorg. allgem. Chem., **136**, p. 62; 1924.
[6] A. Charronat, Compt. rend., **180**, p. 1271; 1925.
[7] H. Gall and G. Lehmann, Ber., **59**, p. 2856; 1926.
[8] Howe, J. Am. Chem. Soc., **49**, p. 2381; 1927.

II. PRECIPITATION BY HYDROLYSIS

The work of Ruff and Bornemann [9] on the determination of osmium suggested the possibility of a somewhat similar method for ruthenium. Ruff and Bornemann precipitated hydrated osmium dioxide by neutralizing an alkaline osmate solution with sulphuric acid.

A few experiments were made with ruthenium, following Ruff and Bornemann's procedure for osmium. Six 10 ml portions of a solution of ruthenium chloride, containing about 0.001 g of ruthenium per milliliter, were made strongly alkaline with sodium hydroxide and allowed to stand on the steam bath for about one hour. The excess alkali was then neutralized with 2 *N* sulphuric acid, using phenolphthalein as indicator. The neutral solutions were allowed to remain on the steam bath for an additional hour before filtering. The precipitates were washed with a hot 1 per cent solution of ammonium sulphate. The quantities of ruthenium recovered were 0.0107, 0.0111, 0.0107, 0.0107, 0.0107, and 0.0106 g, the average being 0.0108 g. The quantities of ruthenium recovered from four 10 ml portions of the same solution, which has been evaporated in crucibles and ignited in hydrogen to metal, were 0.0104, 0.0106, 0.0105, and 0.0105 g, the average being 0.0105 g.

The results are seen to be slightly higher than those obtained by simple evaporation and reduction. Some silica may have been carried down with the precipitated ruthenium, as was observed by Ruff and Bornemann in the case of osmium. It appeared that such contamination might be avoided, as well as that due to the adsorption of alkali, if the neutralization of the ruthenium solution were approached from the acid side. Accordingly, two 10 ml portions of the ruthenium chloride solution were diluted to about 100 ml each, heated to boiling and neutralized with a solution of sodium bicarbonate. The solutions were boiled about 10 minutes. The quantities of ruthenium recovered were 0.0104 and 0.0104 g. It was observed that as the solution approached neutrality a well-coagulated precipitate suddenly appeared, leaving a clear supernatant liquid which was acid to methyl red indicator. Additional bicarbonate and longer boiling produced no further precipitation of ruthenium.

III. EXPERIMENTS TO DETERMINE CONDITIONS FOR COMPLETE PRECIPITATION OF RUTHENIUM BY HYDROLYSIS

In order to avoid errors due to volumetric measurements, weighed portions of the compound, ammonium chlororuthenate, were used in subsequent experiments.

Three preparations of this salt were made. That used in the experiments reported in Table 1 was obtained as the final product of the refining of a large quantity of ruthenium. It was the salt which was precipitated by adding a saturated solution of ammonium chloride to the solution of ruthenium chloride produced by dissolving ruthenium tetroxide in hydrochloric acid. The second preparation, used in the experiments reported in Tables 2, 3, and 4, was made from ruthenium sponge obtained by igniting a portion of the salt, mentioned above, in hydrogen. No impurities were detected in this spongy

[9] O. Ruff and F. Bornemann, Z. anorg. Chem., 65, p. 429; 1910.

metal by spectrographic examination. This sponge was dissolved in a mixture of sodium hydroxide and sodium hypochlorite, according to the directions of Howe and Mercer,[10] and the ruthenium tetroxide distilled into 6 *N* hydrochloric acid. The resulting solution was evaporated, the sirupy residue redissolved in 6 *N* hydrochloric acid, and the filtered solution saturated with chlorine. The relatively insoluble ammonium chlororuthenate, precipitated by the addition of a saturated solution of ammonium chloride, was collected on a hardened filter in a Gooch crucible and washed with 95 per cent alcohol until the washings were colorless. The third preparation, used in the experiments reported in Tables 5 and 6, was made by recrystallizing a portion of the first preparation from a solution containing 2 per cent of hydrochloric acid. No attempt was made to prepare compounds of definite composition. Each preparation was dried over phosphorous pentoxide in a desiccator, then thoroughly mixed by grinding in an agate mortar.

A number of experiments were made to determine the pH of the solutions in which the ruthenium was apparently completely precipitated on boiling with sodium bicarbonate. The ruthenium content of the salt used in the first set of experiments, determined by igniting four portions in hydrogen, ranged from 30.89 to 30.92 per cent, average 30.90 per cent. The ruthenium content of this same salt in the second set, after it had remained a greater length of time in the desiccator, was 30.96 per cent, the individual determinations being 30.97, 30.95, and 30.97 per cent.

Additional samples, simultaneously taken, were each dissolved in about 150 ml of water. The resulting solutions were boiled for about five minutes. A 10 per cent solution of sodium bicarbonate was added dropwise until the colloidal precipitates, which first formed, coagulated and settled. The solutions were then boiled 10 minutes longer and filtered. The filtrates were removed and the filters and precipitates washed with a hot 1 per cent solution of ammonium sulphate until the chloride ion could no longer be detected in the wash waters. The pH of each filtrate, without washings, was determined by the comparison of approximately 10 ml portions with solutions of known pH, using brom cresol purple as indicator. The wash waters, together with unused portions of the filtrates, were evaporated and tested for ruthenium as described in a later section of this paper. No ruthenium was detected in these filtrates and washings.

The filters and precipitates were dried and ignited. The tendency of the precipitates to deflagrate had been observed during the very first experiments. In one instance the deflagration amounted to an explosion which shattered the porcelain crucible and bent the wire triangle on which it rested. The oxidized residues from the ignition of the precipitates were reduced to metal by ignition in hydrogen and weighed.

To determine if there was a significant loss of ruthenium on ignition in air, 0.1094 g of ruthenium sponge was heated in an open crucible with the full heat of the Tirrill burner for three periods of 20 minutes each. At the end of each period the oxidized material was ignited and cooled in hydrogen. The weight obtained in each instance was

[10] See footnote 3, p. 994.

identical with the original weight. In all determinations made throughout this work, both by direct ignition of the salt in hydrogen and by hydrolysis, the weights reported are those obtained after the second ignition period and corrected for the filter ash. This correction amounted to a deduction of 0.0001 g, and was determined from blank runs.

The recoveries in experiments Nos. 11 and 12 are low because a small amount of the precipitate could not be removed from the walls of the beakers. This error is entirely avoided if unetched glassware is used.

The results of the experiments are given in Table 1.

TABLE 1.—*Determination of the pH value of the solution in which ruthenium has been completely precipitated by hydrolysis*

[Ru content: Series I, 30.90 per cent; Series II, 30.96 per cent]

SERIES I

No.	Salt taken	Ru present	Ru recovered	Error	pH of filtrate
	g	g	g	g	
9	0.3529	0.1091	0.1091	0.0000	6.0
10	.3516	.1087	.1087	.0000	6.4
11	.3496	.1081	.1079	−.0002	6.4
12	.3505	.1083	.1080	−.0003	6.3

SERIES II

16	0.3975	0.1231	0.1229	−0.0002	6.2
17	.4137	.1281	.1281	.0000	6.4
18	.4495	.1392	.1391	−.0001	6.0
19	.4622	.1431	.1431	.0000	6.3
20	.4270	.1322	.1322	.0000	6.3

IV. EXPERIMENTS TO DETERMINE BEST CONDITIONS FOR IGNITION OF HYDRATED RUTHENIUM OXIDE

It was found early in the experimental work that great care had to be taken to prevent mechanical loss of ruthenium when the hydrated oxide and the filters were ignited. This loss occurred when the filters were charred. Deville and Stas [11] had experienced the same difficulty with the ignition of hydrated iridium oxide. Ruff and Bornemann [12] encountered similar trouble with hydrated osmium dioxide, obtained by hydrolysis, and attributed the deflagration which occurred to the splitting off of the water as the compound was converted to the anhydrous form.

It was thought that concentrated sulphuric acid present with the dried filters would possibly extract the water from the hydrated ruthenium oxide and in this way prevent deflagration. The results with sulphuric acid, however, were not particularly satisfactory. Deflagration was prevented in some instances, but the results were high, owing probably to the incomplete removal of carbonaceous matter rather than to the retention of sulphur, as no significant amount of sulphur could be found in the metal residues. In other instances deflagration, with simultaneous loss of ruthenium, occurred anyway.

[11] See footnote 1, p. 993.

[12] See footnote 9, p. 995.

Two experiments were made in which the precipitates and filters were merely washed with hot water. On charring the filters these precipitates decrepitated badly.

Precipitates which had been washed with a 1 per cent solution of ammonium sulphate or of ammonium chloride either did not deflagrate or only crackled slightly, with no loss of ruthenium, if the filters were charred slowly. It was observed that if the filters contained a small quantity of either of the salts named they would nearly always char completely when once they began to smoke, without the addition of further heat. Once the filters were charred there was no further danger of deflagration, and the subsequent ignition could be conducted without special precaution.

Since the presence of a small quantity of ammonium sulphate or of ammonium chloride appeared to minimize the danger of loss, somewhat stronger solutions of these salts were tried. These stronger solutions were placed on the filters after complete washing had been accomplished with a hot 1 per cent solution of the particular salt in question. A 5 per cent solution of ammonium sulphate used as a final wash to impregnate the filters, prevented deflagration entirely, even when the filters were charred as in ordinary analytical practice, but the results were somewhat high, similar to those obtained with sulphuric acid. A 5 per cent solution of ammonium chloride likewise prevented deflagration, but the results were low, possibly because of volatilization of some ruthenium as chloride.

A 2.5 per cent solution of either ammonium sulphate or ammonium chloride equally prevented deflagration, even though no special care was taken during the charring, and apparently caused no errors.

The hydrated ruthenium oxide was precipitated from boiling solutions by adding a 10 per cent solution of sodium bicarbonate as previously described, the end point being determined by the presence in the solution of brom cresol purple indicator. The carbonate was added until the color of the brom cresol purple changed from yellowish to faint purple. This change occurs at a pH value of about 6.0. The solutions were boiled 5 to 6 minutes to insure complete precipitation, filtered immediately, and the filters and precipitates washed thoroughly with a hot 1 per cent solution of either ammonium sulphate or of ammonium chloride. Stronger solutions of these salts were then applied as indicated in the following tables. No ruthenium was detected in the filtrates from these precipitations by tests described in the following section of this paper.

The ruthenium salts used were the second and third preparations previously described. The ruthenium content of Preparation II, obtained by direct ignition of 12 portions taken at random from among the samples weighed, ranged from 30.40 to 30.44 per cent and averaged 30.42 per cent. The ruthenium content of Preparation III, the recrystallized salt, obtained by direct ignition of four portions in hydrogen, ranged from 31.22 to 31.26 per cent and averaged 31.24 per cent.

The results of the experiments in which hot water was used for washing and in which sulphuric acid was used to char the filters are given in Table 2.

TABLE 2.—*Effect of washing with water and of charring with* H_2SO_4

No.	Salt taken 30.42 per cent Ru	Ru present	Ru recovered	Error	Remarks
	g	*g*	*g*	*g*	
5	0.4524	0.1376	0.1324	−0.0052	Washed with hot water; loss by deflagration.
6	.4080	.1241	.1239	−.0002	
9	.4408	.1341	.1347	+.0006	Washed with hot 1 per cent $(NH_4)_2SO_4$; charred with H_2SO_4; probably incomplete removal of carbon; no deflagration.
10	.4599	.1399	.1402	+.0003	
11	.4497	.1368	.1333	−.0035	Washed with hot water; charred with H_2SO_4; loss by deflagration.
12	.4383	.1333	.1330	−.0003	

The results of the experiments in which a hot 1 per cent solution of ammonium sulphate and of ammonium chloride were used for washing and in which the filters were carefully charred are given in Table 3.

TABLE 3.—*Effect of careful charring by heat*

No.	Salt taken 30.42 per cent Ru	Ru present	Ru recovered	Error	Remarks
	g	*g*	*g*	*g*	
1	0.4202	0.1278	0.1279	+0.0001	Washed with hot 1 per cent $(NH_4)_2SO_4$; careful charring by heat; no deflagration.
2	.4303	.1309	.1309	.0000	
3	.5593	.1701	.1702	+.0001	
4	.5187	.1578	.1578	.0000	
17	.4790	.1457	.1457	.0000	
28	.3601	.1095	.1097	+.0002	Washed with hot 1 per cent NH_4Cl; careful charring by heat; no deflagration.
29	.3626	.1103	.1103	.0000	

The results of the experiments in which 5 per cent solutions of ammonium sulphate and of ammonium chloride were used are given in Table 4.

TABLE 4.—*Prevention of deflagration by presence of ammonium salts*

No.	Salt taken 30.42 per cent Ru	Ru present	Ru recovered	Error	Remarks
	g	*g*	*g*	*g*	
13	0.5007	0.1523	0.1527	+0.0004	Washed with hot 1 per cent $(NH_4)_2SO_4$; final wash with 5 per cent $(NH_4)_2SO_4$; no special precaution taken in charring; no deflagration.
15	.5325	.1620	.1623	+.0003	
18	.4337	.1319	.1322	+.0003	
19	.4453	.1355	.1356	+.0001	
26	.3379	.1028	.1023	−.0005	Washed with hot 1 per cent NH_4Cl; final wash with 5 per cent NH_4Cl; no special precaution taken in charring; no deflagration; possibly slight volatilization as chloride.
27	.3955	.1203	.1197	−.0006	

The results of the experiments in which 2.5 per cent solutions of ammonium sulphate and of ammonium chloride were used, with no special precaution taken to char the filters, are given in Table 5. The results of two experiments with 1 per cent ammonium sulphate in which the filters were carefully charred are likewise included.

TABLE 5.—*Best conditions for ignition of ruthenium precipitate*

No.	Salt taken 31.24 per cent Ru	Ru present	Ru recovered	Error	Remarks
	g	*g*	*g*	*g*	
2	0.2722	0.0850	0.0850	0.0000	Washed with hot 1 per cent $(NH_4)_2SO_4$; careful charring; no deflagration.
3	.3384	.1057	.1057	.0000	
41	.4562	.1425	.1426	+.0001	Washed with hot 1 per cent $(NH_4)_2SO_4$; final wash with 2.5 per cent $(NH_4)_2SO_4$; no special precaution taken in charring; no deflagration.
42	.5329	.1665	.1666	+.0001	
40	4891	.1528	.1527	−.0001	Washed with hot 1 per cent NH_4Cl; final wash with 2.5 per cent NH_4Cl; no special precaution taken in charring; no deflagration.
43	.5001	.1562	.1561	−.0001	

V. EXAMINATION OF FILTRATES FROM HYDROLYSIS FOR PRESENCE OF RUTHENIUM

All of the filtrates in the foregoing experiments were carefully examined for the presence of ruthenium. The tests which were used were made as follows:

1. DEVELOPMENT OF A GREEN OR BLUISH-GREEN COLOR BY REACTION WITH THIOUREA

Chugaev,[13] in his researches on osmium compounds, discovered a reaction which serves as a delicate test for osmium. He found that when a solution containing osmium tetroxide or potassium chloroösmate, acidified with a few drops of hydrochloric acid, is heated with thiourea ($CS(NH_2)_2$) for a few minutes a deep red or rose color develops. The limit of sensitivity, according to Chugaev, appears to be 1 part in 100,000 parts of solution.

It was observed in this laboratory that thiourea also develops a color with ruthenium solutions under conditions similar to those specified by Chugaev for osmium. The color with ruthenium is green or bluish-green, depending upon the concentration of the ruthenium. The limit of sensitivity appears to be the same as that for osmium. The test becomes uncertain, however, if the ruthenium solution has been treated with nitric acid or with aqua regia.

2. DEVELOPMENT OF A PINK OR ROSE COLOR BY REACTION WITH SODIUM THIOSULPHATE

This delicate test was discovered by C. Lea,[14] who found that when an ammoniacal solution of ruthenium chloride is heated for a few minutes with sodium thiosulphate ($Na_2S_2O_3$), a permanent pink or rose color develops, depending upon the concentration of the ruthenium. The limit of sensitivity of this test likewise appears to be 1 part in 100,000 parts of solution. In using this test it was observed that previous treatment of the solution with nitric acid or with aqua regia had no effect upon the development of the color.

The filtrates and wash waters from the experiments reported in Table 1 were evaporated to dryness, moistened with a few drops of hydrochloric acid, diluted to 5 ml, and heated with a few crystals of

[13] L. Chugaev, Compt. rend., **167**, p. 235; 1918.
[14] Cited by William Crookes, Select Methods in Chemical Analysis (Longmans, Green & Co.), p. 463; 1894.

thiourea. No green color was observed. Solutions containing 0.0001 g of ruthenium were simultaneously tested. These solutions did develop a distinct color.

The filtrates and wash waters from the experiments reported in Tables 2, 3, 4, and 5 were evaporated to dryness and the brom cresol purple indicator present destroyed by evaporation with concentrated nitric acid. The nitric acid was destroyed by repeated evaporation with concentrated hydrochloric acid before testing with thiosulphate. No pink color was detected in the solutions of the evaporated filtrates. Solutions containing 0.0001 g of ruthenium were similarly treated and did develop the characteristic pink color.

VI. PRECIPITATION OF RUTHENIUM FROM SOLUTIONS CONTAINING POTASSIUM CHLORIDE

A few experiments were made to ascertain whether the presence of alkali chlorides would cause any error in the determination of ruthenium by hydrolysis.

The determinations were made as has been previously described, care being taken to wash the filters and precipitates until no chloride ion could be detected in the wash waters. The filters and precipitates were finally washed four to five times with a 2.5 per cent solution of ammonium sulphate to prevent deflagration on ignition. In experiments Nos. 1 and 2 the precipitates were redissolved in 6 *N* hydrochloric acid after they had been washed only partially. These solutions, freed from paper pulp, were evaporated to eliminate the excess of acid, diluted to a volume of 150 ml, and the ruthenium reprecipitated.

The details of the experiments are condensed in Table 6.

TABLE 6.—*Determination of ruthenium by hydrolysis in presence of potassium chloride*

No.	Salt taken	Ru present	Ru recovered	Error	Remarks
	g	*g*	*g*	*g*	
1	0.4546	0.1420	0.1420	0.0000	Ru content of salt used, 31.24 per cent; 10 per cent KCl present; 2 precipitations.
2	.5228	.1633	.1631	−.0002	
3	.4407	.1377	.1377	.0000	Ru content of salt used, 31.24 per cent; 10 per cent KCl present; single precipitation.
4	.3461	.1081	.1082	+.0001	
5	.6110	.1891	.1891	.0000	Ru content of salt used, 30.94 per cent; 0.7 per cent KCl present.

NOTE.—All 5 of the metal residues were leached with hot water. There was no change in weight, except in experiments Nos. 3 and 4, each of which lost 0.0001 g.

VII. DETERMINATION OF RUTHENIUM IN ALKALINE SOLUTIONS

As stated in the introduction to this paper, an alkali hydroxide may be used to absorb the ruthenium tetroxide set free by distillation. Two experiments were made to ascertain whether any error in the determination was introduced by having made the solution of ruthenium alkaline.

Two 10 ml portions of a solution of ruthenium chloride, equivalent to 0.0105 g of ruthenium, were each made strongly alkaline with a freshly prepared solution of sodium hydroxide. The solutions were

boiled gently for about three minutes, then cooled and acidified with a large excess of hydrochloric acid. The solutions were evaporated to dryness, diluted to a volume of 150 ml with water and the ruthenium precipitated by hydrolysis. The quantities of ruthenium recovered were 0.0104 and 0.0105 g.

VIII. BEHAVIOR OF RUTHENIUM WHEN PRESENT AS A NITROSOCHLORIDE

In the preceding experiments the ruthenium was present as the chloride or as ammonium chlororuthenate. From solutions of such compounds the complete precipitation of ruthenium by hydrolysis is easily accomplished. If the solution of ruthenium chloride has been evaporated with considerable alcohol, thus causing the reduction of the ruthenium to the tervalent stage, ruthenium can be quantitatively precipitated under the conditions described, but the precipitate is somewhat slow in settling and, in general, is not as easy to handle as the quadrivalent compound.

A few experiments were made with solutions in which the ruthenium was present, partly if not entirely, as nitrosochloride ($RuCl_3NO$). This type of compound results when solutions of ruthenium are subjected to a somewhat prolonged treatment with nitric acid or with aqua regia and forms an important class of ruthenium compounds. It was found that solutions containing ruthenium as nitrosochloride yielded only a slight precipitate which appeared to have a tan color rather than the black usually observed.

Several different treatments were tried, qualitatively, in an attempt to remove the nitroso radicle. In one a boiling acidified solution of the nitrosochloride was saturated with a current of chlorine. In another the solution was made strongly alkaline with sodium hydroxide and boiled. In a third the solution was made alkaline, sodium peroxide added, and boiled. None of these treatments was at all effective.

Wichers,[15] in his experiments on the separation of rhodium from platinum, had observed the incomplete precipitation of ruthenium when solutions of the nitrosochloride were boiled with a suspension of barium carbonate. He concluded that the solution as prepared really contained a mixture of chloride and nitrosochloride, and that the former compound was hydrolyzed with complete precipitation while the latter precipitated only slightly if at all.

IX. BEHAVIOR OF RUTHENIUM WHEN PRESENT AS AN AMMINE

A solution of ammonium chlororuthenate which had been made ammoniacal and boiled, then acidified with hydrochloric acid and neutralized with sodium bicarbonate, gave only a small amount of black precipitate. The greater portion of the ruthenium remained in solution, imparting to it a dark color. Such a behavior was to be expected, since the platinum metals are transformed in ammoniacal solution into ammines, some of which are very stable.

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[15] E. Wichers, J. Am. Chem. Soc., **46**, p. 1818; 1924

X. SUMMARY OF RESULTS OBTAINED

1. Ruthenium, when present as a chloride, can be quantitatively precipitated as a hydrated oxide from a boiling solution having a pH value of about 6.0. If present as nitrosochloride or as ammine only a slight precipitation occurs.

2. There is a tendency to deflagrate, with accompanying loss of ruthenium, when the hydrated oxide is converted by heat into the anhydrous oxide. This tendency is minimized if the filters contain a small quantity of either ammonium sulphate or ammonium chloride. The quantity of salt retained when the filters and precipitates are washed with a 2.5 per cent solution of either of the salts named appears to be sufficient to overcome the danger of deflagration.

3. The presence in the solution of alkali chlorides, such as potassium chloride, introduces no appreciable error into the determination. The alkali chloride may be completely removed from the precipitate by washing.

4. There is no significant loss of ruthenium on ignition in air, with the full heat of the Tirrill burner, during the time required in the analysis, namely, one hour.

5. The detection of ruthenium in solution is readily accomplished by reaction with thiourea. The limit of sensitivity appears to be 1 part in 100,000 parts of solution.

XI. THE METHOD

1. PRECIPITATION

Use clean unetched beakers. Adjust the volume of the solution so that it contains not more than 0.2 g of ruthenium in 150 ml. If necessary, acidify with hydrochloric acid. If the ruthenium solution has been evaporated with a considerable quantity of alcohol, add 5 ml of freshly prepared chlorine water and boil. In any case, heat the faintly acid solution just to boiling and add a 10 per cent solution of sodium bicarbonate, free from insoluble matter, until a precipitate suddenly coagulates. Add a few drops of brom cresol purple indicator. Then add sufficient bicarbonate solution to produce a faint purple color, boil five to six minutes, and filter immediately. Wipe the inner walls of the beaker and also the glass stirring rod with a small piece of filter paper to remove adhering precipitate. Wash thoroughly with a hot 1 per cent solution of ammonium sulphate. Finally wash three or four times with a cold 2.5 per cent solution of ammonium sulphate.

2. IGNITION

Place the filter and precipitate in a porcelain crucible and char the paper somewhat slowly. The dried filter will usually char completely when once it begins to smoke. Ignite the residue to remove all carbonaceous matter.

3. REDUCTION

Cover the crucible with a Rose lid, preferably of quartz. Introduce into the crucible a stream of hydrogen, burning from the tip of a Rose delivery tube (a quartz tube is preferred). After five

minutes remove the burner and a few minutes later extinguish the hydrogen flame by momentarily breaking the current of hydrogen. This is best done by having a section of the rubber delivery tube replaced by a glass tube, one end of which can easily be disconnected. Allow the ruthenium to cool in an atmosphere of hydrogen and weigh as metallic ruthenium.

Acknowledgment is made to Edward Wichers for many helpful suggestions.

WASHINGTON, June 14, 1929.

RP126

OBSERVATIONS ON THE IRON-NITROGEN SYSTEM

By S. Epstein, H. C. Cross, E. C. Groesbeck, and I. J. Wymore

ABSTRACT

By means of thermal analyses, microscopic examinations, and X-ray analyses of nitrided electrolytic iron specimens a study has been made of the iron-nitrogen system. From the data obtained and with the diagrams of Sawyer and Fry as a basis, a modified iron-nitrogen constitution diagram has been tentatively drawn. The upper temperature horizontal noted by Sawyer was also observed, but this has been ascribed to a peritectoid instead of a eutectoid transformation. Three nitrided layers were observed, whereas Fry noted only two. The three layers have been designated as Fe_2N, Fe_4N, and Fe_8N. Observations on several specimens of aluminum molybdenum nitriding steel are also described.

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I. INTRODUCTION

From the standpoint of nitriding, the constitution diagram of the iron-nitrogen system is important, mainly because it must form the basis of our understanding of the more complex system involved in the nitriding of the special alloy steels. No practical use has been made, or is very likely to be made, of nitrided pure iron. The iron-nitrogen system may conveniently be divided into two parts—one of a low nitrogen content corresponding with the core of nitrided articles and one of a much higher nitrogen content, corresponding with the case.

The low-nitrogen side of the diagram is of general importance, since it is believed that comparatively small amounts of nitrogen may materially affect the mechanical properties of iron and steel. According to the diagram as determined by Fry,[1] the iron-nitride constituent, familiar to metallographers in its characteristic needle form, is appreciably soluble in iron in the temperature range 500° to 550° C. and much less soluble at room temperature. This suggested to Griffiths [2] that nitrogen may be a factor in the temper brittleness of steel and he obtained evidence tending to support this view. More recently, Dean, Day, and Gregg [3] showed, as was predicated by

[1] Fry, A., Stickstoff in Eisen, Stahl und Sonderstahl. Stahl und Eisen, **43**, p. 1271, 1923; Kruppsche Monatshefte, **4**, p. 138; 1923.
[2] Griffiths, W. T., Note on Nitrogen as Possible Factor in Temper Brittleness, J. Iron & Steel Inst., **111**, p. 257; 1925.
[3] Dean, R. S., Day, R. O., and Gregg, J. L., Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-Nitrogen, Technical Publication No. 193, A. I. M. M. E.; 1929.

Sawyer,[4] that the needlelike iron-nitride constituent causes precipitation or dispersion hardening in iron and therefore likewise suggested that temper brittleness and blue-heat phenomena in iron may be due to nitrogen. An investigation of the iron-nitrogen system by Murakami and his associates has been announced,[5] in which two compounds on the iron side of the diagram have been found by means of magnetic analysis and microscopic examination. Only the results of the X-ray studies were available in published form at the time the bureau report was written.

The accurate determination of the iron-nitrogen diagram, especially for alloys of high nitrogen content, is extremely difficult. Fairly homogeneous alloys of iron and nitrogen of very low nitrogen content can be obtained by melting iron in an atmosphere of nitrogen, but alloys of high nitrogen content can not be produced in this way, even under very high pressures of nitrogen. Under a pressure of 3 atmospheres Sawyer [6] obtained an alloy of 0.034 per cent [7] nitrogen content, under 200 atmospheres Andrew [8] obtained an alloy of 0.3 per cent nitrogen, and according to a calculation by Sawyer under 900 atmospheres an alloy of 0.6 per cent should be obtained. According to Sawyer's calculation, the constant, 0.02, multiplied by the square root of the nitrogen pressure gives the percentage of nitrogen in the alloy. Since the nitrogen pressure enters into this formula as the square root it will be apparent, that, if even the formula is approximately correct, obtaining very high nitrogen content in iron by melting under pressure is hardly practicable.

The usual method of introducing nitrogen into iron is by diffusion into hot solid iron; molecular nitrogen does not diffuse appreciably, and nascent nitrogen, such as is formed by "cracking" ammonia gas by passing it over hot iron, is necessary. In this way iron-nitrogen alloys containing a maximum of about 11 per cent nitrogen may be produced. However, the nitriding is not uniform, but takes place by the formation of several distinct layers of different iron-nitrogen compounds and constituents, so that the chemical composition of even a very small nitrided particle may vary discontinuously from a small fraction of a per cent near the center to the maximum of about 11 per cent nitrogen at the surface. The difficulty of determining and interpreting critical points in such specimens by a precise method, such as thermal analysis, is manifest. Moreover, there is the added difficulty that the nitride layers are very unstable, nitrogen gas being liberated upon heating to temperatures as low as 300° C. and the gas evolution increasing rapidly at higher temperatures. Thus, during a thermal analysis the chemical composition of the specimen is always changing, and the heat effects produced by the gas evolution may obscure transformation points or be mistaken for them. The fact that the iron-nitrogen alloys decompose when heated makes it practically impossible to obtain homogeneous specimens by annealing, except with those of comparatively low nitrogen content. The

[4] Sawyer, C. B., Nitrogen in Steel. Trans. Am. Inst. Min. & Met. Eng. **49**, p. 799; 1923. The Reactions and Effects of Nitrogen in Steel, Trans. A. S. S. T., **8**, p. 291; 1925.

[5] Osawa, A., and Iwaizumi, S., X-ray Investigation of Iron and Nitrogen Alloys, Sci. Repts., Tohoku Imperial Univ., Sendai, Japan; Series I, **18**, No. 1, 1929.

[6] Sawyer, C. B., Nitrogen in Steel, Trans. A. I. M. M. E., **49**, p. 799; 1923.

[7] All percentage figures for nitrogen used herein are by weight, not by volume.

[8] Andrew, J. H., The Influence of gases upon the Critical Ranges of the Iron Carbon Alloys, Iron & Steel Inst. Carnegie Schol. Mem., **3**, p. 236, 1911; Iron and Nitrogen, J. Iron & Steel Inst., **86**, p. 210; 1912.

determination of the iron-nitrogen diagram by the use of nitrided specimens may be likened to a hypothetical study of the iron-carbon diagram in which only carburized specimens were available, wherein not only one iron-carbide was formed but two or more, and in which much of the carbon escaped on heating and cooling.

Early in 1922, before either Sawyer's or Fry's work was published, the Bureau of Standards began a series of thermal analyses of nitrided specimens. While it soon became evident that thermal analysis alone is insufficient for establishing the relationships between iron and nitrogen, the work was continued as time permitted. Within the last year, however, the work has been more active and an attempt has been made, with the diagrams of Sawyer and Fry as a basis, supplemented by microscopic and X-ray examinations, together with the thermal analysis data, to resurvey some portions of the iron-nitrogen system.

No claim whatever is made that the present paper completely settles the iron-nitrogen constitution diagram. Some of the interpretations of the data are matters of opinion. In a system beset with so many difficulties, final conclusions can not be hastily drawn.

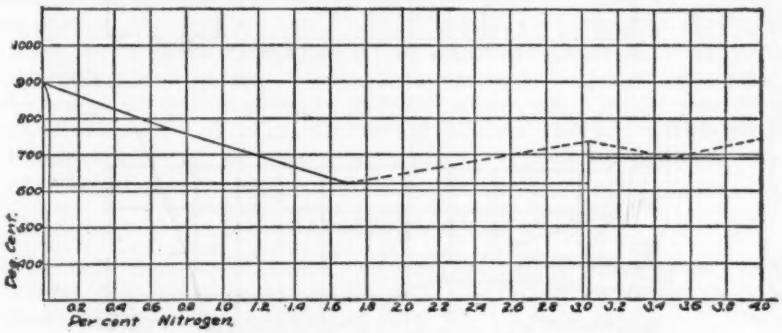

FIGURE 1.—*Sawyer's iron-nitrogen constitution diagram*

II. DISCUSSION OF SAWYER'S AND FRY'S DIAGRAMS

A brief discussion may here be given of the two existing diagrams of the iron-nitrogen system determined independently by Sawyer [9] and by Fry [10] at about the same time, in 1923. These diagrams are shown in Figures 1 and 2. Sawyer depended largely on thermal analysis, which he supplemented by microscopic examinations. Fry, on the other hand, in view of the previously mentioned difficulties involved in thermal analysis, avoided this method entirely and relied mainly on microscopic examinations. Fry worked with a 0.1 per cent carbon steel and Sawyer with very low carbon sheet iron.

On the lower nitrogen side of the diagram Sawyer and Fry are in substantial agreement. The diagram in this region closely resembles the iron-carbon diagram. Nitrogen, like carbon, lowers the A_3 point of iron and a eutectoid, Braunite,[11] a constituent named for one of the first to study this system, occurs similar to pearlite

[9] See footnote 6, p. 1006.
[10] See footnote 1, p. 1005.
[11] Braune, H., Influence De L'Azote Sur Le Fer et L'Acier, Rev. de Métallurgie, **2**, p. 498, 1905; **4**, p. 834; 1907. Stahl und Eisen, Ueber die Bedeutung des Stickstoff's im Eisen, **26**, p. 1357; 1906.

in steel, but contains about twice as much nitrogen as the carbon content in pearlite. Sawyer placed the nitrogen content of Braunite at 1.7 per cent, Fry at 1.5 per cent. The eutectoid horizontal in the iron-nitrogen system is about 100° C. lower than in the iron-carbon system. Sawyer placed it at 620° C. and Fry at 580° C. The solid solubility of nitrogen in iron at room temperature is quite

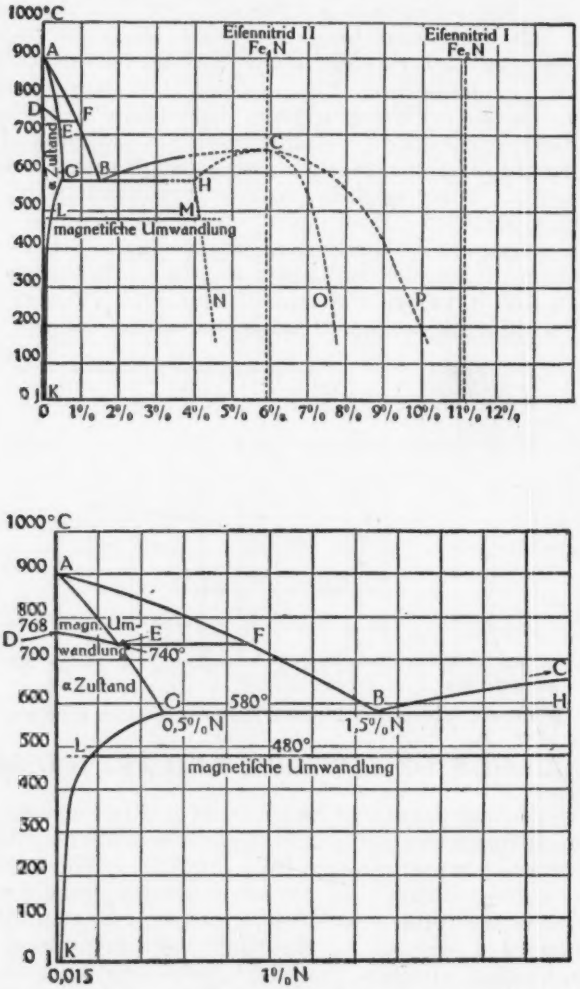

FIGURE 2.—*Fry's iron-nitrogen constitution diagram*

low, Sawyer placed it at 0.03 per cent and Fry at 0.015 per cent. This is somewhat higher than the solubility of carbon in iron at room temperature which is considered to be below 0.01 per cent.[12] Sawyer did not determine the solubility of nitrogen at the eutectoid horizontal, but Fry sets this at the very appreciable value of 0.5 per cent; in this respect there is considerable difference between the

[12] Gillett, H. W., discussion of paper by M. A. Grossman on Oxygen Dissolved in Steel, and Its Influence on the Structure, presented at A. S. S. T. convention, 1928.

behavior of carbon and nitrogen, since the solubility of the former at the A_1 point is not very much higher than at room temperature, it being generally placed at about 0.035 per cent.

For alloys of higher nitrogen content Sawyer's and Fry's diagrams are at considerable variance, as may be briefly pointed out. Sawyer considered the nitrogen compound, which together with iron, forms the eutectoid, Braunite, to be Fe_8N whereas Fry considers it to be Fe_4N. Sawyer, from his thermal analyses and from microscopic evidence which will be discussed later, decided that there was another eutectoid transformation, which takes place at 690° C. between the compounds Fe_8N and Fe_6N. Fry's diagram does not contain this horizontal. Sawyer did not continue his diagram beyond the compound Fe_6N (4 per cent nitrogen), but Fry also included the compound Fe_2N (11.3 per cent nitrogen), which he indicated to be unstable.

Murakami concluded from his recent studies [13] that there are two iron-nitrogen compounds, Fe_2N and Fe_4N, corresponding to nitrides I and II described by Fry. His interpretation of the complete diagram is not yet available, however.

Fry also made magnetic measurements and placed a magnetic transformation horizontal across the lower nitrogen side of the diagram at 480° C. Indications of thermal transformations, in the form of "swings" instead of definite arrests, in this temperature range were obtained in the bureau's thermal analyses, but it is not certain that the magnetic transformation had any relationship to the low temperature "swings." The interpretation of these thermal effects was not sufficiently clear, however, to warrant representing them on the constitution diagram.

III. THERMAL ANALYSES

In order to obtain as uniform distribution of nitrogen as possible, Sawyer nitrided thin disks of sheet iron 0.228 mm thick which he piled on top of one another to form his thermal analysis specimens. At the bureau, after some preliminary work with solid pieces of iron, it was decided to use electrolytic iron crushed, before nitriding, into granules to pass through a 20-mesh sieve and in later work through a 30-mesh sieve.

The electrolytic iron cathodes used as raw material were first cleaned with hydrochloric acid if the surface was oxidized, washed with water and with alcohol, dried, and pulverized in a steel mortar to pass a 30-mesh sieve. In order to reduce any oxide present, the powdered iron was heated to 900° C. in oxygen-free and dry hydrogen for three hours or 950° C. for two hours and allowed to cool in the hydrogen. In nitriding, a 40 g sample of the reduced iron was placed in a thin layer in an alundum boat in an electric tube furnace, a thermocouple being inserted into the charge for temperature control.

A stream of very pure ammonia gas, further purified by passing through two towers, one containing soda lime and the other solid caustic potash, was passed through the furnace tube to displace the air. The furnace was then heated to the desired temperature, held there for the desired length of time, and the sample allowed to cool in the furnace, the flow of ammonia being maintained through the whole cycle. A flow gage at the exit end of the tube allowed maintenance of a constant flow of the gas.

[13] See footnote 5, p. 1006.

In some of the experiments the samples, after nitriding, were heated in an atmosphere of nitrogen at definite temperatures and for a known period of time. Commercial nitrogen was passed over hot copper in a second tube furnace to remove oxygen, then through a phosphorus pentoxide tube for removal of water, and then through the soda lime and caustic potash towers and over the specimen in the tube furnace of the apparatus above described.

In order to obtain a compact specimen and to insure close contact with the thermocouple tip in the thermal analysis, the powdered nitrided iron was compressed in a steel die under 75,000 lbs./in.^{2} pressure, into briquettes 0.26 by 0.32 by 0.50 inch. Specimens with an average nitrogen content of 2.4 per cent or less were strong enough so that they could be slotted with a hacksaw and handled as a solid specimen. With higher nitrogen, the briquettes would crumble in the fingers; hence the thermal runs on specimens showing 2.5 to 5 per cent nitrogen by analysis were made on the pulverulent samples packed tightly about the thermocouple bead in a small alundum crucible which was kept tightly covered.

Table 1 shows the conditions of nitriding and the nitrogen content of samples prepared, and also the time and temperature of heating for the specimens which were annealed in nitrogen.

TABLE 1.—*Nitriding conditions for specimens for thermal analyses*

Specimen No.	Nitriding conditions		Annealing		Nitrogen content [1]
	Temperature	Time at temperature in NH_3	Temperature	Period at temperature in nitrogen	
	°C.	Hours	°C.	Hours	Per cent by weight
21	400	½			0.02
23	400	1			.14
28	400	¾			.30
18	450	1			.20
8	450	3			[2] .21
22	500	¼			.27
27	500	½			.81
29	500	½			.95
24	500	¾			2.12
25	550	¼		[3]	.65
20	550	½			1.41
26	550	1			[4] 2.47
7	550	2			3.00
5a	650	1			4.80
6	650	1			2.40
9	650	4			2.69
10	650	5			3.43
17	650	8			3.35
13		½	650	½	[5] .50
14		¾	650	¾	1.30
15		¼	650	¼	[6] 1.25
16		1	650	1	1.25
4	650	1	600	1	.19
3		1	750	1	.015
2		1	850	1	.02
1		1	950	1	.03
5		1	950	1	.01

[1] All nitrogen determinations, here and elsewhere, were made by L. Jordan, chemist, and associates.
[2] Sample 8, after thermal analysis (maximum temperature of thermal analysis run, 875° C.), contained 0.18 per cent nitrogen.
[3] Not annealed.
[4] Sample 26, after thermal analysis (maximum temperature of thermal analysis run, 1,030° C.), contained 0.04 per cent nitrogen.
[5] Sample 13, after thermal analysis (maximum temperature of thermal analysis run, over 930° C.), contained 0.20 per cent nitrogen.
[6] Sample 15, after thermal analysis (maximum temperature of thermal analysis run, 967° C.), contained 0.02 per cent nitrogen.

The amount of nitrogen taken up is obviously dependent on both time and temperature. It is probable also that the rate of flow through or the pressure in the furnace may influence the degree of nitriding. These factors were maintained as constant as possible, although the control was by no means perfect. With few exceptions (notably Nos. 5a and 14, and No. 4), the series is fairly self-consistent. In general, it appears that nitriding at 550° C. is nearly as rapid as at 650° C. It may be concluded from Table 1 that decomposition on heating in nitrogen at or below 650° C. was slow, but that at 750° C. or above it was rapid, being almost complete in an hour.

As shown in Table 1, sample No. 8, nitrided three hours at 450° C. (0.21 per cent nitrogen), retained almost all its nitrogen (0.18 per cent) after thermal analysis, and No. 13, containing 0.50 per cent nitrogen after being nitrided one-half hour at 650° C. and heated one-half hour in nitrogen at 650° C., retained 0.20 per cent after thermal analysis. This specimen, however, gave evidence of evolution of nitrogen while passing through its critical point at 600° C. as shown by the flow meter registering the passage of the stream of nitrogen out of thermal analysis tube.

On the other hand, No. 15, initially containing much more nitrogen than No. 13, showed almost none after thermal analysis, and No. 26 with about 2½ per cent nitrogen initially, lost almost all of this during thermal analysis. It seems, therefore, that an iron-nitrogen alloy produced by nitriding till only a low nitrogen content is attained is more stable on heating than the alloys corresponding to a relatively large percentage of nitrogen.

It is evident that, on account of decomposition during the heating run, the cooling curves will not all represent the initial nitrogen content and that most of the cooling curves may represent iron which is practically nitrogen-free. The decomposition might also be expected to change the compactness and size of the briquette so that less intimate thermal contact might result between thermocouple bead and briquette in the upper part of the heating curve as well as on the cooling curve.

The inverse rate thermal analysis apparatus and methods used at the Bureau of Standards have been described by Scott and Freeman [14] and by French.[15]

The thermal curves obtained with the unannealed specimens listed in Table 1 are shown in Figure 3. No effect due to nitrogen was visible with 0.02 per cent nitrogen. With 0.14 per cent nitrogen a definite point appeared at about 600° to 620° C. With 0.21 per cent nitrogen the low temperature swing appeared on a run not reproduced in Figure 3, the 600° to 620° C. point also appearing. With 0.27 per cent only the 605° C. point appeared. With 0.30 per cent nitrogen a sharp low temperature swing occurred, but the lower part of the curve is of doubtful reliability, as it does not show the proper shape. The point appearing at 590° to 620° C. was shown by all subsequent curves, through 0.95 per cent nitrogen.

With 1.41 per cent nitrogen the 590° to 620° C. point appeared and a higher temperature point also. With 2.40 per cent nitrogen the

[14] Scott, H., and Freeman, J. R., jr., Use of a Modified Rosenhain Furnace for Thermal Analysis, B. S. Sci. Paper No. 348, 1919.
[15] French, H. J., A Recording Chronograph for the Inverse-Rate Method of Thermal Analysis, B. S. Tech. Paper No. 230, 1923.

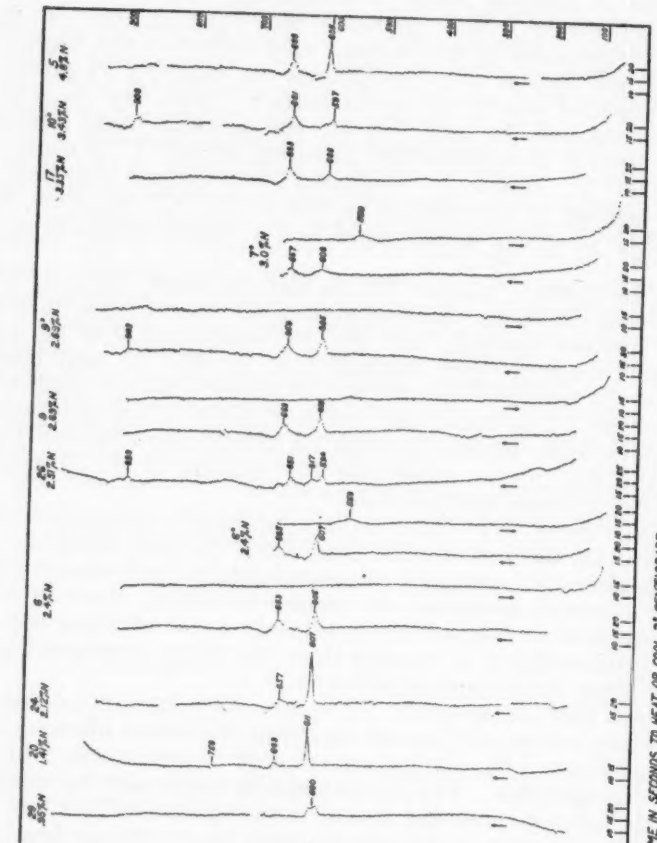

FIGURE 3.—*Thermal analysis curves of nitrided electrolytic iron granules*

These specimens were not annealed in nitrogen after the nitriding treatment.

cooling curve (specimen No. 6, fig. 3), like those of all the lower nitrogen specimens of this series taken after the temperature has been raised to 900° C. or above, showed no effect of nitrogen. A duplicate (first) run on a second sample of No. 6° carried only to 670° C. showed a point on cooling (fig. 3), thus indicating that there is a certain reversibility of the thermal effect due to nitrogen if the nitrogen is not lost by decomposition. Throughout the rest of the series the 590° to 620° C. point and the higher temperature point that first appeared with 2.40 per cent nitrogen were observed.

The thermal curves obtained with specimens annealed in nitrogen after nitriding (Table 1) are shown in Figure 4. The results obtained with samples containing 0.03 per cent nitrogen or less are not consistent. In this range of nitrogen content, if the specimens were uniform throughout each grain, according to Sawyer, the nitrogen would be in solid solution at all temperatures, and, according to Fry, would be in solid solution above 400° C.

With samples of a higher nitrogen content, No. 4 (0.19 per cent nitrogen), Figure 4, doubtful swings and sharply marked double points were noted. This was heated only to 675° C. and the cooling curve again showed a doubtful swing. No. 13 with 0.50 per cent nitrogen was one of the most interesting specimens. A point of marked intensity, comparable to A_1, was observed which strongly indicated the presence of a definite eutectoid. On duplicate runs the heating curves of Nos. 13 and 13° (fig. 4) gave identical results, but the cooling curves showed no sign whatever of any effect of nitrogen. During the heating of Nos. 13 and 13°, copious evolution of nitrogen took place as the sample passed through the point at 600° C.

The average nitrogen content of this specimen, 0.50 per cent, happens to coincide with the limit of solubility of nitrogen in ferrite at 0.50 per cent shown by Fry. The temperature, however, was 605° C. against Fry's figure of 580° C., established by quenching and metallographic examination of the quenched specimens rather than by heating curves. Since the 0.50 per cent refers to average nitrogen content, it is not likely that the specimen really represents that composition on Fry's diagram.

The critical ranges on heating found in the unannealed nitrided series of Figures 3 and of the nitrided and annealed series of Figure 4 are shown in Figure 5, in which circles show the maxima of the runs on samples not annealed and crosses those of the annealed series. The length of the vertical lines shows the width of the temperature range. The points group themselves, for specimens with 1.25 per cent nitrogen and above, quite definitely about two temperatures, 660° and 605° C., and the ranges always pass through those temperatures.

It will be observed that the A_3 point in alloys of high initial nitrogen content is very much weaker in both heating and cooling curves than is normal for electrolytic iron, and that while the method appears sensitive enough to show A_2 even on briquetted specimens, in many cases neither A_2 nor A_3 was detected.

Nitriding in the nitrogen-hydrogen mixture resulting from the cracking of ammonia might be expected to result in the removal by hydrogen of the carbon and oxygen present in electrolytic iron. The upper end of the heating curve and the cooling curve should, therefore, represent iron more or less purified from carbon and

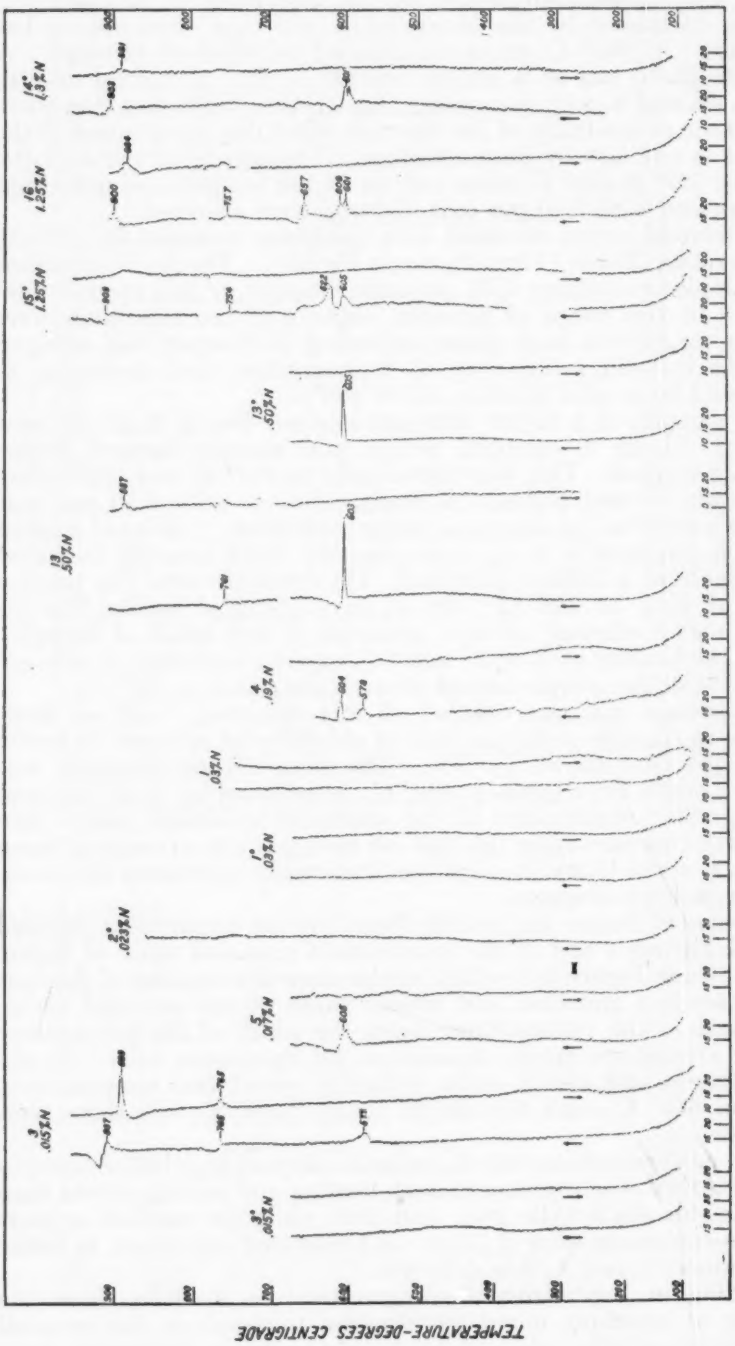

FIGURE 4.—*Thermal analysis curves of nitrided electrolytic iron granules*

These specimens were annealed in nitrogen after the nitriding treatment.

oxygen, but contaminated with some nitrogen. Since Yensen [16] argues that pure iron free from carbon and oxygen should have no transformations, these thermal analyses indicate that Yensen's hypothesis deserves respectful consideration.

As shown in Figure 5, Sawyer's two arrests in higher nitrogen alloys were confirmed. The lower one, which undoubtedly represents the Braunite eutectoid transformation, may be set from these results at 605° C. The upper horizontal which occurred only in alloys of average composition, 1.25 per cent nitrogen or higher, may be set at 660° C. As will be discussed later, microscopic examination indicated that this upper transformation could not be due to another eutectoid on the higher side of the diagram as Sawyer decided, but that it was probably due to a peritectoid reaction above the eutectoid horizontal.

Another point on which the thermal analyses throw some light is the solid solubility of nitrogen in iron. In iron containing 0.2 per cent average nitrogen (specimen 4, fig. 4) the arrest in the eutectoid transformation range was not sharp, as in iron containing 0.5 per cent average nitrogen (specimen 13, fig. 4), but was doubled. A possible interpretation of this is that the lower portion of the double transformation represents the solution of the nitride in alpha iron and the upper portion the eutectoid transformation of that zone of the specimen having a higher nitrogen content. If this view is correct, it would indicate appreciable solubility of nitrogen in iron at the eutectoid transformation temperature, and thus partly substantiate Fry's figure of 0.5 per cent. That a definite arrest was obtained in the specimen of 0.5 per cent average nitrogen content can not be considered as evidence that no more than this content is soluble, because of the lack of uniformity in the composition of the specimens. In this range the average nitrogen content appears to be roughly only about a third of that of the outer layer.

IV. MICROSCOPIC EXAMINATION

In examining under the microscope sections of the granules used in the thermal analyses the two layers described by Fry as Nitride I and Nitride II and considered by him to be solid solutions of the compounds Fe_2N and Fe_4N, respectively, were recognized. However, no eutectoid between the two layers was found such as Sawyer reported. His explanation that the upper horizontal shown by thermal analysis represented a eutectoid transformation can only hold if such a eutectoid exists. The other possible way of accounting for the upper horizontal—namely, that it represents a peritectoid reaction—is therefore suggested. Such an explanation, however, calls for the presence of another compound, as shown in Figure 20. In examining blocks of remelted electrolytic iron specially nitrided for the purposes of microscopic examination, an extreme outer layer not hitherto observed in the granules and not described by Fry was detected. At first this surface layer was thought to be due to oxide resulting from moisture in the ammonia gas used, but as it still appeared after the ammonia had been dried with metallic sodium, it was decided to be another nitride layer. The support this gave to the supposition that the upper horizontal represented a peritectoid reaction was

[16] Yensen, T. D., Pure Iron and Allotropic Transformations. Tech. Pub., 185, Amer. Inst. Min. & Met. Engrn.; February, 1929.

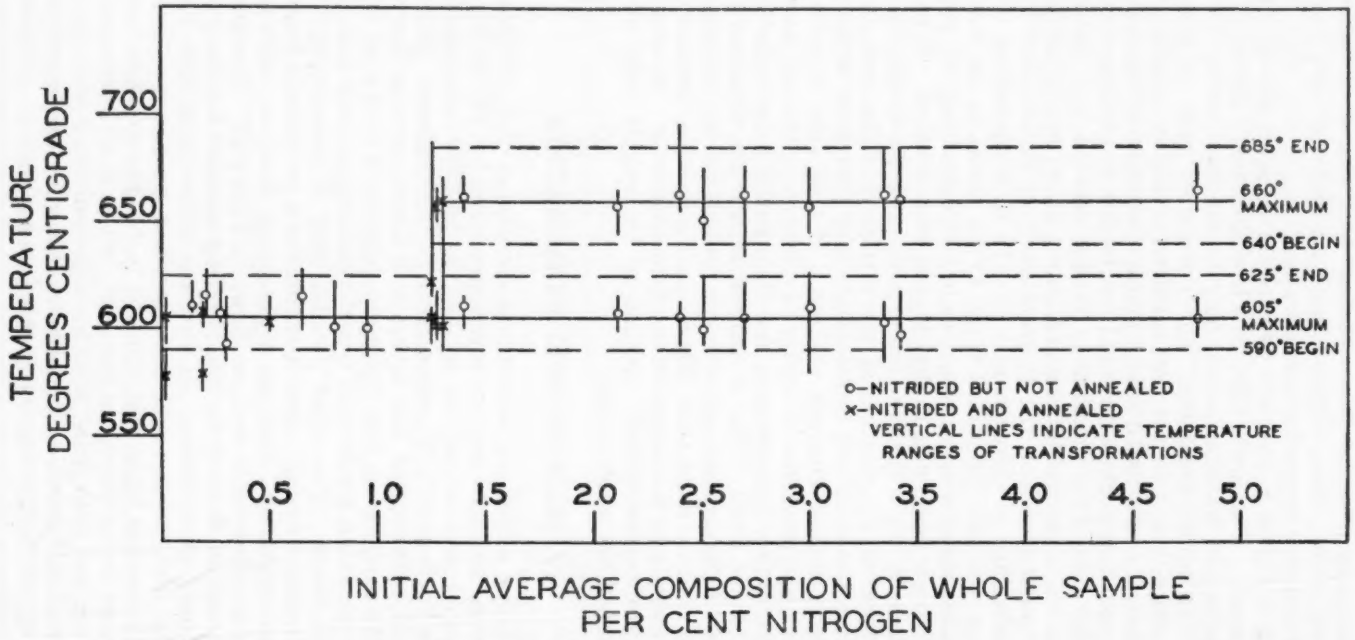

FIGURE 5.—*Summary of thermal analysis curves*

The points indicate arrests on the inverse rate heating curves.

recognized, and the regions in the diagram on both sides of this line were explored by microscopic examination for further confirmation.

The details of the microscopic examination will now be described. Figure 6 shows the appearance of sections through the granules of two thermal analysis specimens. The structures shown are representative, in regard to uniformity and depth of nitriding, of all the thermal analysis specimens. The nitrogen penetration was not uniform, most of it being concentrated in the surface layers.

Figure 7 shows the structure of a specimen which chemical analysis showed to contain only 0.01 per cent average nitrogen. The presence of what appear to be nitride needles is of interest, for it may indicate that the solid solubility of nitrogen in iron may be lower than the value, 0.015 per cent, given by Fry. It should be remembered, however, that too great reliance can not be placed in the values obtained for nitrogen content due to lack of homogeneity of the specimens.

The layers designated in Fry's micrographs as Nitride I and Nitride II may be seen in Figure 8, the thicker outer layer being Nitride I. The outer layer is light brown in color and is not appreciably attacked by 5 per cent alcoholic picric acid. The thin inner layer is a lighter cream color, is attacked by picric acid, and also is colored dark brown by boiling sodium picrate; it exhibits twinning as was noted by Fry and Sawyer. A characteristic of this inner layer, which apparently has not been previously noted, is its marked tendency to form slip lines, as shown. These probably arose when the granules were compressed into the briquettes used for thermal analysis. It appeared evident from the etching characteristics of the nitride needles that, as has also been noted by Fry, they are composed of the same constituent as the inner layer.

In the specimens nitrided below 600° C. only the two layers and the nitride needles were present. In those nitrided above 600° C., however, the eutectoid, Braunite, also appeared. This is the dark constituent, resembling pearlite, shown in Figure 9. It always appeared on the interior side of Nitride II; without doubt, Braunite is a eutectoid of this compound and iron. Figure 9 (*b*) depicts a nitrided specimen annealed in vacuum at 685° C., after which it contained 0.5 per cent average nitrogen. The specimen was composed of approximately one-third eutectoid, and this, therefore, roughly confirms Sawyer's and Fry's values for the eutectoid composition of 1.5 per cent nitrogen.

Thus far only the structures of the electrolytic iron granules used for thermal analysis have been considered. Since it was difficult to prepare these granules satisfactorily for microscopic examination, small blocks of remelted electrolytic iron were nitrided and used. These were mounted in solder before polishing so that the sections could be observed to the extreme edge. The specimens were not ground on an abrasive wheel but were smoothed on emery paper laid on a board, this precaution being taken in order not to break off the nitrided layers.

In these nitrided blocks an outer layer not described by Fry, lying outside the layer designated in his micrographs as Nitride I, was detected. The appearance of this layer, which has a eutectoid structure, is shown in Figures 10 and 11; in these and subsequent figures the outer nitride layer is at the top or at the left of the micro-

graphs. In examining nitrided electrolytic iron specimens received from another laboratory, the outside layer was observed and found to contain an oxide constituent as shown in Figure 12. It is evident, however, that the whole outer layer can not be attributed to oxide since, as previously mentioned, specimens nitrided in ammonia completely freed from moisture showed the outer layer. The color of the lamellæ and globules present in the outer layer, in the unetched state somewhat resembles that of iron oxide although the layer is considerably lighter and can readily be distinguished from iron oxide by etching.

This extreme outer layer was not noted by Fry, perhaps, on account of the rounding and cracking of the edges of his polished sections, but more probably because at the high temperature (680° C.) at which the specimens shown in his micrographs were nitrided the outer constituent is decomposed and only voids and fissures remain in its place. This is indicated by some of Fry's micrographs. The "decomposed appearance" of the structure of the outer layer upon nitriding at 600° C. or higher is shown in Figure 13.

Since this newly found layer has a eutectoid structure, the question may arise whether it is not the eutectoid which Sawyer considered to be formed at the upper horizontal. The evidence indicated very strongly, however, that this is not so. The layer is at the extreme outside and can not, therefore, be a eutectoid between the two inner nitride compounds as indicated in Sawyer's diagram. Moreover, the eutectoid structure of this outermost layer is already well marked at temperatures as low as 425° C. (see fig. 10 (*b*)), much below the temperature of the upper horizontal (660° C.). In fact, upon heating to a temperature as high as this the eutectoid structure of the outer layer disappears, due to decomposition.

A number of specimens were heated above the temperature of the upper horizontal and slowly cooled, but, as shown in Figures 14 and 15, no eutectoid could be detected between the two inner nitride layers, as is required by Sawyer's diagram. That these specimens had actually passed through a transformation, upon heating to the temperatures used in these tests, was evident from the disappearance of the inner layer (fig. 16 (*c*)) upon quenching the specimens above the transformation temperature. According to Sawyer's diagram, on the assumption of a eutectoid transformation, this inner layer should not disappear on heating to a temperature above the transformation, except at the exact eutectoid composition itself. On the assumption of a peritectoid transformation, however, as shown in Figure 20 the inner layer should disappear entirely on heating through the transformation. This evidence, therefore, together with the fact that three layers were found as called for in the construction of a diagram such as Figure 20, involving a peritectoid transformation, indicated strongly that the upper temperature horizontal represented a peritectoid transformation.

Figure 17 shows the results of tests made to determine the upper solubility or "stability" limit of the most stable nitride layer, namely, the yellowish layer not attacked by picric acid or sodium picrate, designated by Fry as Nitride I. Upon heating in an atmosphere of ammonia to 785° C., this layer still remained undecomposed, but at 815° C. the structure after quenching showed that decomposition was practically complete. The solubility or decomposition limit may,

FIGURE 6.—*Nonuniform penetration of nitrogen in nitrided electrolytic iron granules used for thermal analyses,* × *100*

The etching reagent in all of the micrographs was 5 per cent picric acid in alcohol, unless otherwise stated. *a*, Specimen No. 7 nitrided at 550° C. for two hours; average nitrogen content 3 per cent. It was evident that the bulk of the nitrogen in this specimen was concentrated in the thin surface layers; *b*, specimen No. 13 nitrided at 650° C. for one-half hour; average nitrogen content 0.5 per cent.

FIGURE 7.—*What appear to be nitride needles in a specimen very low in nitrogen,* × *500*

Specimen 5a nitrided at 950° C. for one hour, then annealed at 950° C. in nitrogen for one hour; average nitrogen content 0.01 per cent.

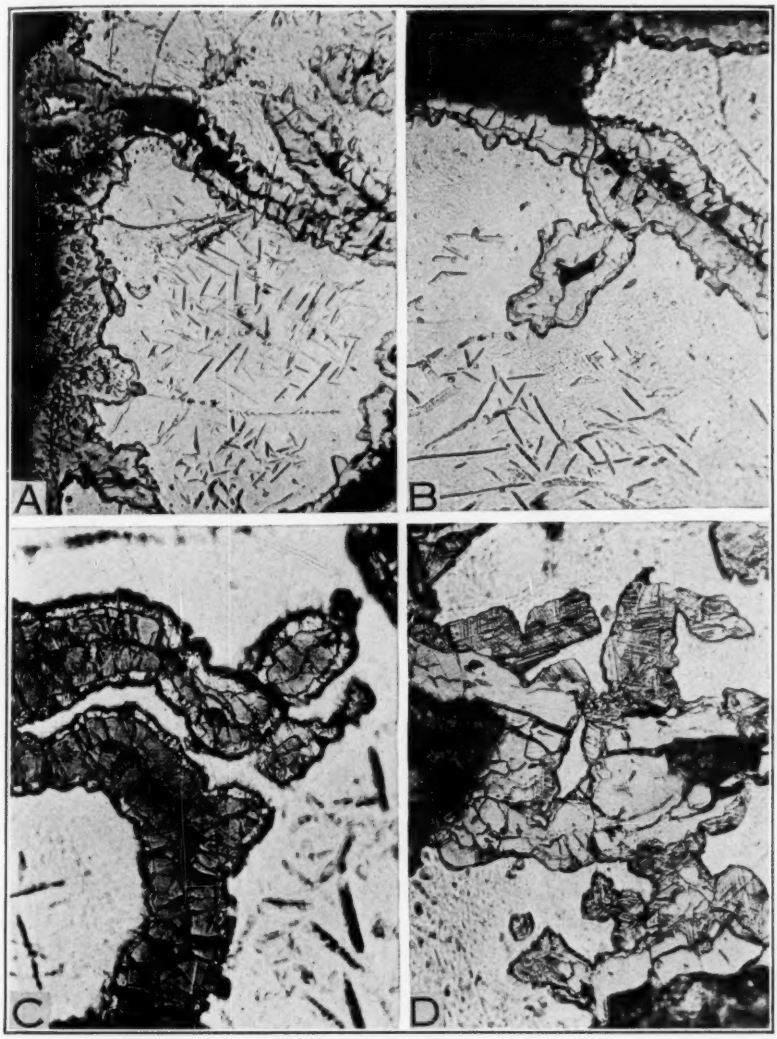

FIGURE 8.—*Layers in nitrided electrolytic iron granules*

a, Specimen No. 7 nitrided at 550° C. for two hours; there is a fairly thick outer layer, and a thin ribbon of an inner layer can be distinguished, × 250; *b*, same as *a*, × 500; *c*, the same specimen more deeply etched. This micrograph was taken not at the surface of the granule, but at a crevice along which the nitrogen penetrated. The "inner layer" is, of course, the one adjacent to the electrolytic iron (the pure white constituent containing the nitride needles and somewhat out of focus) while the "outer layer" extends on both sides of the crevice. Even after the rather prolonged etching the outer layer remained unattacked. In the inner layer what appears to be a twinned structure can be distinguished, × 500; *d*, specimen No. 10 nitrided at 550° C. for five hours. The outer layer may be recognized by its smooth appearance; it is not attacked by the etching solution. The inner layer is covered with a series of slip lines.

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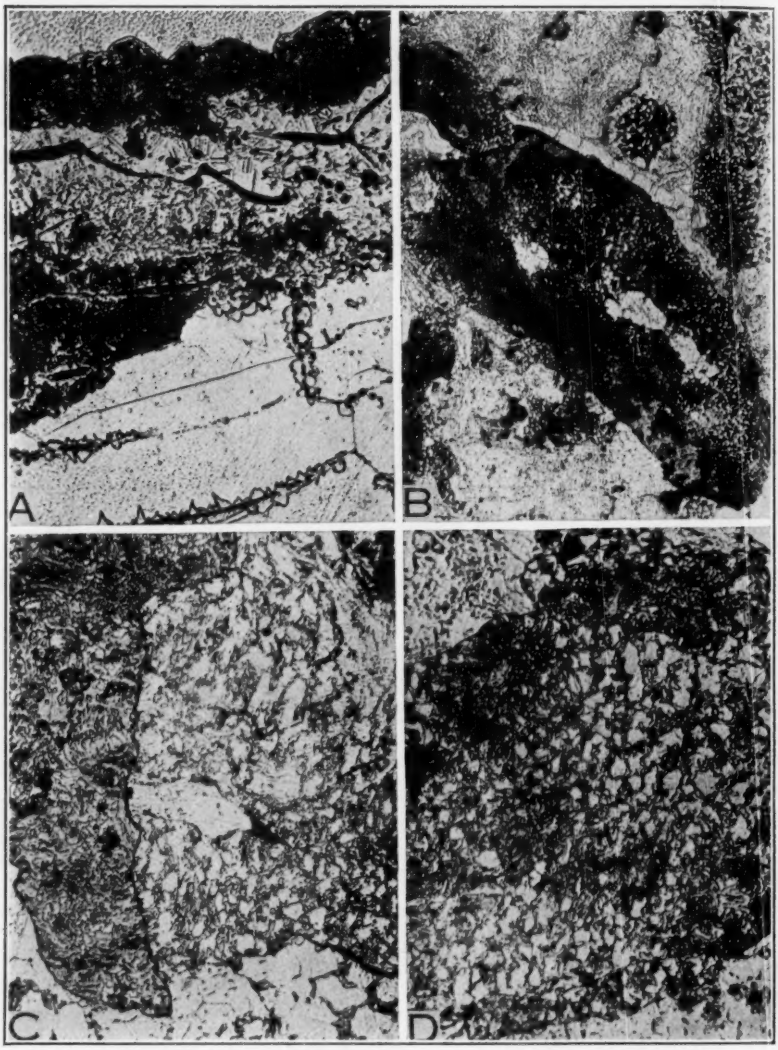

FIGURE 9.—*The eutectoid braunite containing about 1.5 per cent nitrogen*

a, Specimen No. 6 nitrided at 650° C. for one hour; average nitrogen content 2.4 per cent, × 500. The background at the top and bottom of the micrograph is the core of electrolytic iron. The dark constituent is the eutectoid braunite. The white constituent, appearing as a layer showing twins and as the sharply defined globular particles strung along the cracks and grain boundaries at the bottom of the micrograph is the "inner layer"; *b*, specimen No. 10 nitrided at 550° C. for five hours and then annealed at 685° C. in vacuum; average nitrogen content 0.49 per cent, × 100; *c*, same as *b*, × 500; *d*, specimen No. 9 nitrided at 650° C., then annealed at 685° C. in vacuum. The dark constituent is braunite.

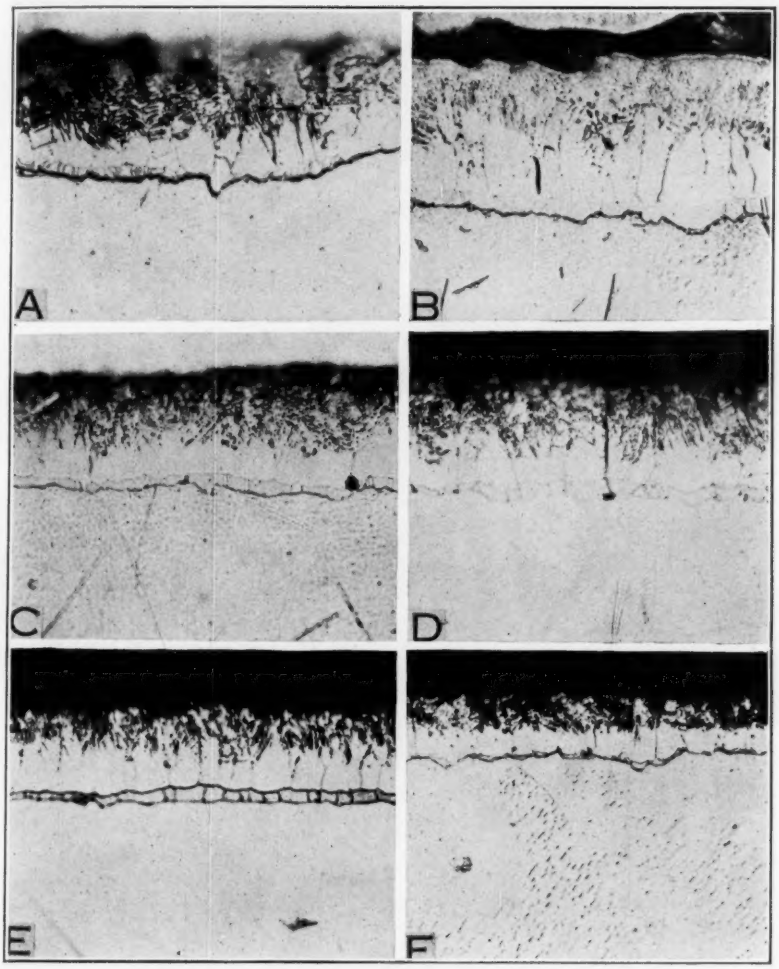

FIGURE 10.—*Appearance of nitrided layers in remelted electrolytic iron blocks, × 500*

Three distinct nitride layers can be distinguished. The extreme outer layer has previously not been noted. As may be seen below, the nitriding temperatures of the specimens which showed a well-defined extreme outer layer were rather low, 550° C. or lower. *a*, Nitrided 75 hours at 500° C.; *b*, nitrided 25 hours at 550° C.; *c*, nitrided 25 hours at 550° C.; *d*, nitrided 75 hours at 500° C., etched in alkaline sodium picrate; *e*, nitrided 25 hours at 550°C.; etched in alkaline sodium picrate; *f*, nitrided 170 hours at 425° C. Boiling alkaline sodium picrate etches the inner layer brown or dark brown depending on the length of etching. The extreme outer layer has the appearance of a eutectoid and is etched by both picric acid and sodium picrate.

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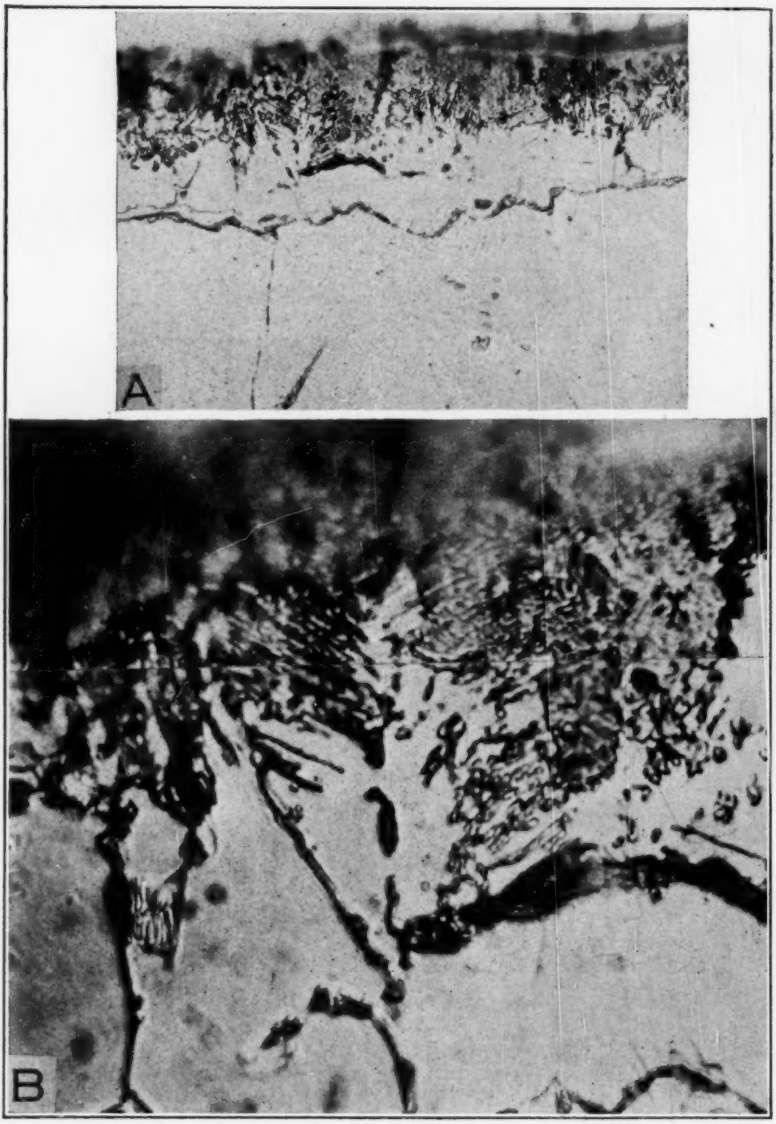

FIGURE 11.—*Appearance of extreme outer layer of nitrided iron block*

a, Nitrided 75 hours at 500° C., × 500; *b*, same spot, × 2,000.

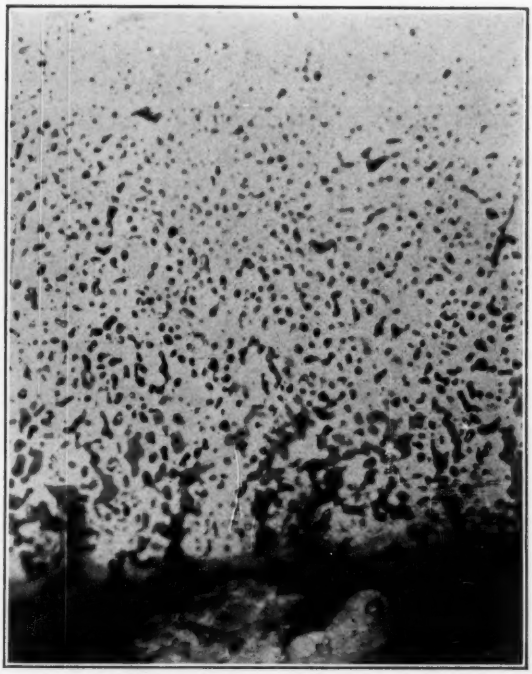

FIGURE 12.—*Oxide constituent at surface of nitrided iron block,* × *500*

The edge of the specimen is at the left side. The dark gray constituent lining the cracks and voids was evidently iron oxide.

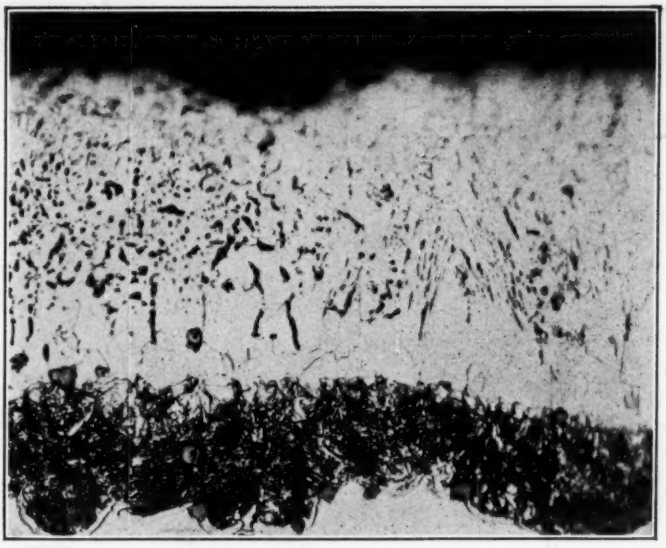

FIGURE 13.—*Apparent decomposition of extreme outer nitride layer,* × *500*

Nitrided 25 hours at 600° C. The voids and fissures in the extreme outer layer indicate the decomposition of the outermost constituent.

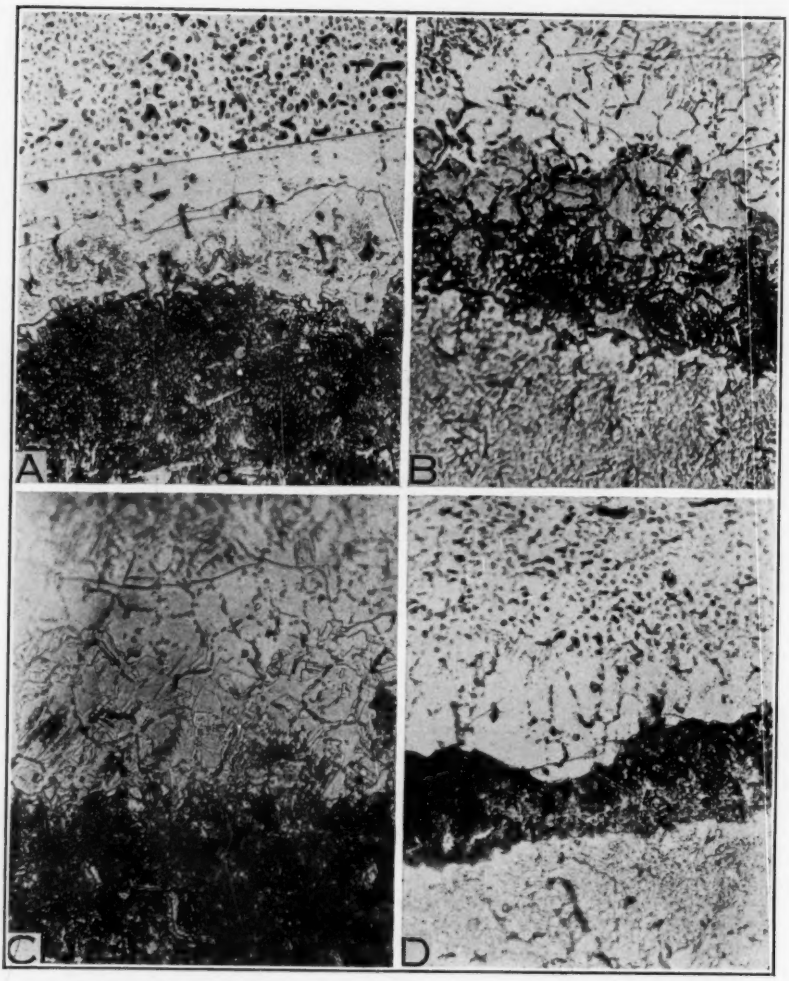

FIGURE 14.—*Appearance of nitrided iron blocks heated above upper horizontal and slowly cooled,* × *500*

a, Nitrided 25 hours at 600° C., then heated one-half hour in NH_3 at 685° C. and furnace cooled; *b*, same as *a*, etched with sodium picrate; *c*, nitrided 75 hours at 500° C., then heated one-half hour in NH_3 at 685° C. and furnace cooled; *d*, same as *c*, etched with sodium picrate. At the bottom of each micrograph the eutectoid braunite is shown; this etches darker with picric acid than with sodium picrate; the inner nitride layer is etched a dark brown by the latter reagent. No signs of the formation of a eutectoid between the two inner nitride layers can be detected.

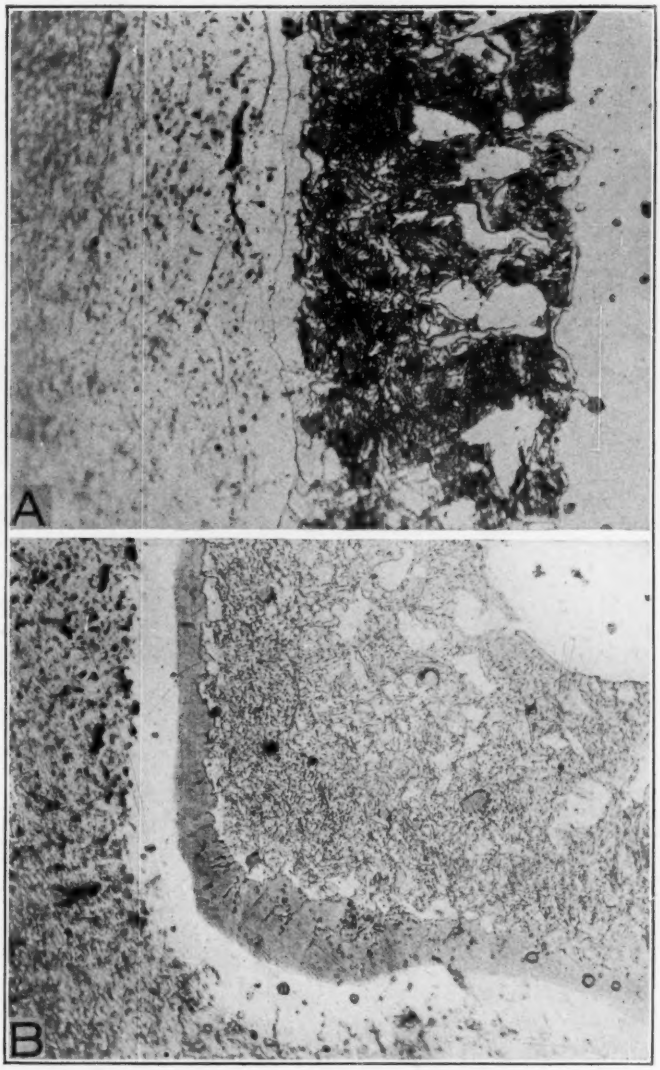

FIGURE 15.—*Appearance of nitrided iron blocks heated above upper horizontal and slowly cooled,* × *500*

a, Nitrided 50 hours at 500° C., then heated one-half hour in NH_3 at 725°C., and furnace cooled. The edge of the specimen is at the left; *b*, nitrided 25 hours at 600° C., then heated one-half hour in NH_3 at 725° C. and furnace cooled; etched with sodium picrate. It is quite plain that no eutectoid was formed between the two inner nitrided layers.

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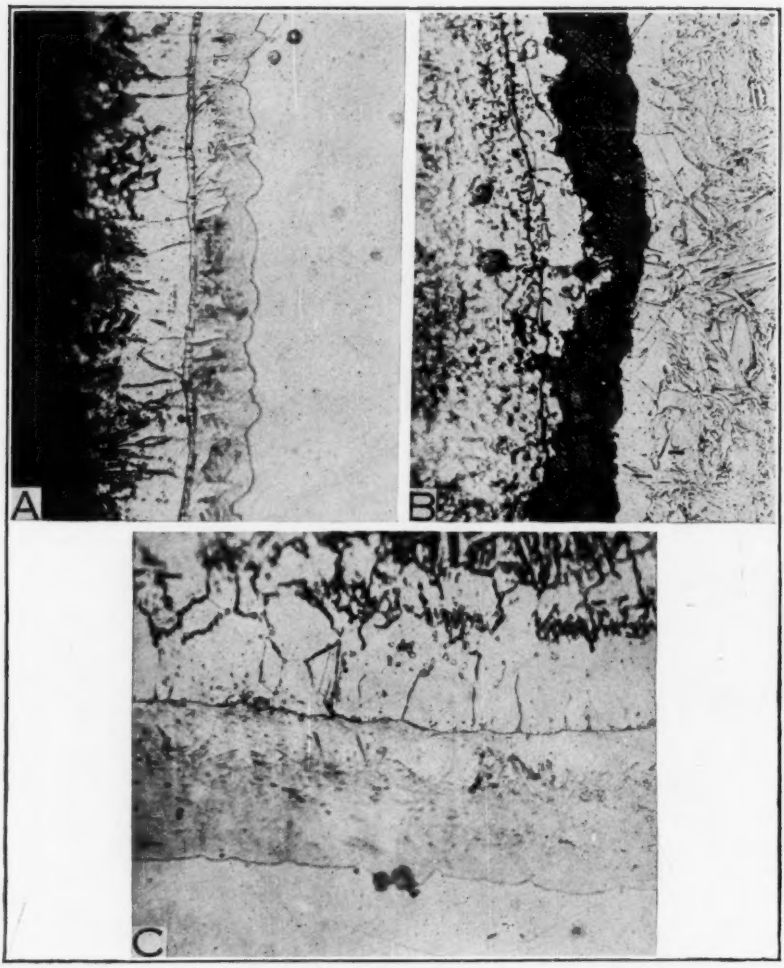

FIGURE 16.—*Appearance of specimens quenched from below and above upper horizontal,* × *500*

Etched with sodium picrate. *a*, Nitrided 75 hours at 500° C., then heated for one-half hour in NH_3 at 625° C., and quenched in water. The thin layer is the inner compound; the layer to the right corresponds to the eutectoid layer, but is martensitic due to quenching. A similar layer is shown in the other two micrographs of this figure; *b*, nitrided 75 hours at 500° C., heated to 685° C. in NH_3, slowly cooled to 625° C., held at this temperature for one-half hour and water quenched. The inner layer darkly etched and showing slip lines is again present, having become a good deal wider as a result of the heating to 685° C; *c*, nitrided at 500° C. for 75 hours, heated to 685° C. for one-half hour in NH_3, and quenched in water. The inner layer which etches dark with sodium picrate is no longer present.

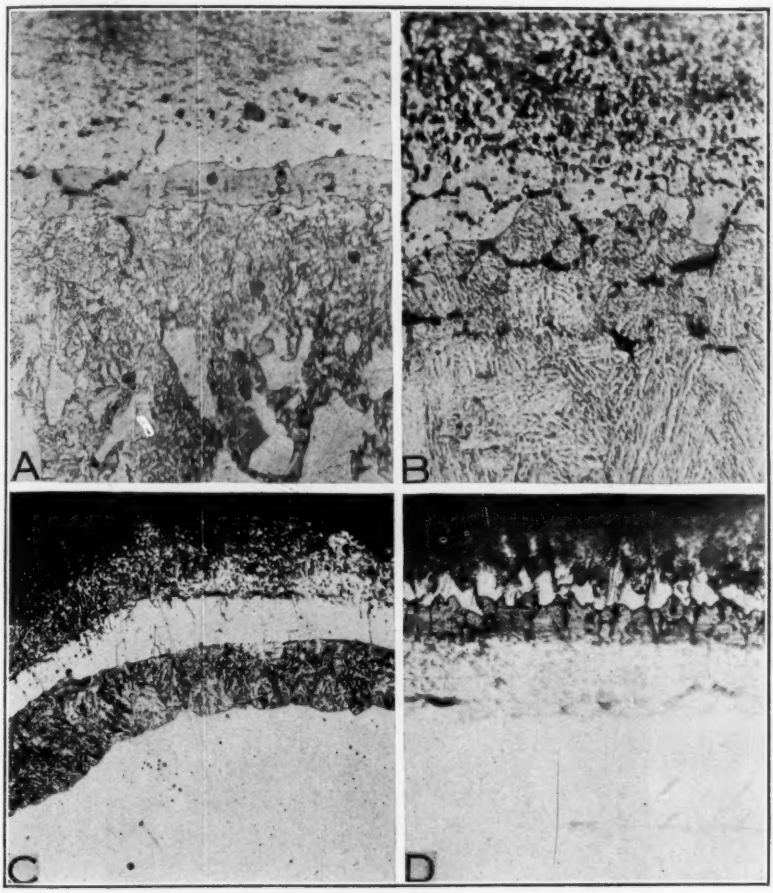

FIGURE 17.—*Determination of upper solubility limit of the more stable nitride layer*

a, Nitrided 75 hours at 500° C., then heated in NH_3 at 785° C. for one-half hour and slowly cooled in furnace; etched with sodium picrate. The lighter colored nitride layer is still intact, × 500; *b*, same as *a*, but quenched in water from 785° C. The light colored layer is still intact, × 500; *c*, nitrided 75 hours at 500° C., heated one-half hour in NH_3 at 815° C. and quenched in water. The middle layer of the three shown is ferrite, indicating decomposition of the nitride layers, × 100; *d*, nitrided 75 hours at 500° C., heated one-half hour in charcoal at 625° C.; the nitride layers appear to be stable, × 500.

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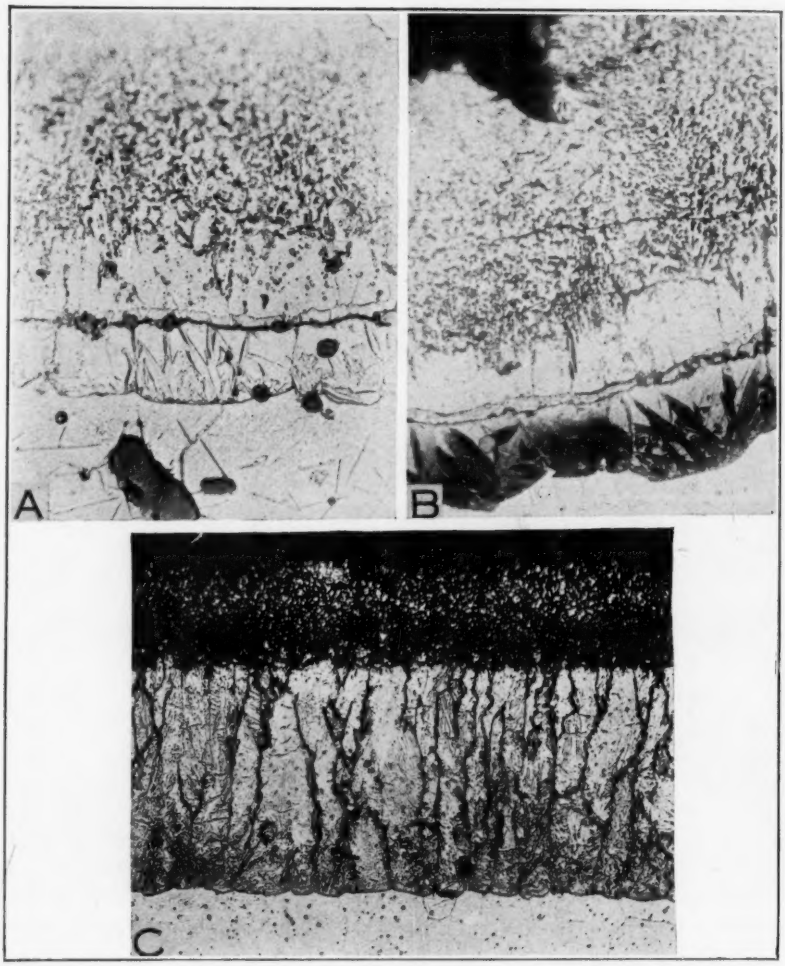

FIGURE 18.—*Martensitic structures obtained on cooling in air from above braunite eutectoid line*

a, Nitrided 25 hours at 600° C., air cooled, × 500; *b*, same as *a*, etched with sodium picrate; *c*, nitrided 25 hours at 700° C., and air cooled, × 100.

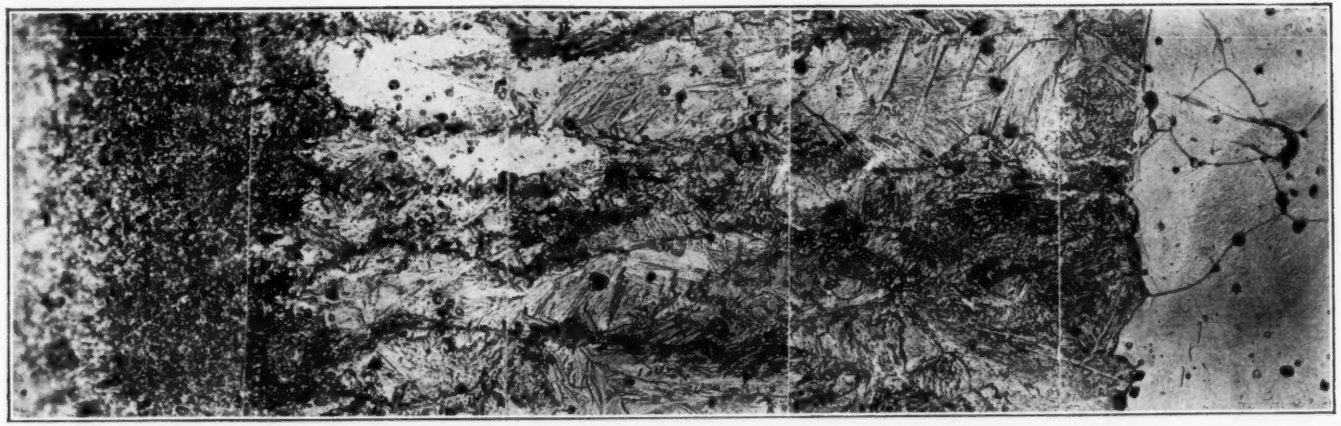

FIGURE 19.—*Same as Figure 18 c,* × *500*

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therefore, be placed at about 800° C. Nitride layers are undoubtedly more stable in an atmosphere of ammonia than in the absence of ammonia. Figure 17 (*d*) shows the structure of a nitrided specimen, packed in charcoal, heated to 625° C., and slowly cooled. The two inner nitride layers were stable at this temperature even in the absence of ammonia.

Figures 18 and 19 show the martensitic condition which forms in the Braunite layer upon fairly rapid cooling in air. The martensitic needles due to nitrogen appear to be very similar to those in carbon steel. The structures shown in Figure 19 also indicate that just as the forms of martensite differ in high and low carbon steels, so in this "nitrogen martensite" the structure toward the higher nitrogen side of the layer is noticeably different from that toward the lower nitrogen side. In high carbon steels austenite is usually retained with the martensite and analogously in the nitrogen alloy the structure of the higher nitrogen side of the layer shown in Figure 19 also indicates the presence of an austenitic constituent.

V. X-RAY DIFFRACTION ANALYSES

X-ray analyses of the crystal structure of several of the specimens of nitrided electrolytic iron granules and of the nitrided electrolytic iron blocks were made by using a General Electric Co. X-ray diffraction apparatus and molybdenum *K* alpha radiation. Particles of the nitrided granules which passed through a 100-mesh sieve were examined by the powder method. The use of the block specimens, which were obtained primarily for the purposes of microscopic examination, for X-ray examination was necessitated by the lack of other corresponding material in a form better adapted for producing satisfactory diffraction patterns. The diffraction patterns of the blocks were obtained by directing the primary X-ray beam at a small grazing angle with the polished surface. Some nitrided specimens of aluminum-molybdenum nitriding steels, kindly supplied by the Molybdenum Corporation, were also analyzed. Table 2 gives a summary of the results.

It will be seen in Table 2 that all the specimens gave the hexagonal close packed pattern except the iron specimens Nos. 13 and 39. This latter specimen, shown in Figures 18 (*c*) and 19, apparently does not contain the intermediate nitride layer discussed in the microscopic examination. The fact that the hexagonal close-packed pattern appeared in the iron specimens nitrided at 600° and 700° C. would indicate that the hexagonal close-packed lines which were obtained can not be due entirely to the outermost layer described in the microscopic examination, since, as has been pointed out, this layer is decomposed at these temperatures. On the other hand, it has been shown that the intermediate layer is stable at these and higher temperatures. The hexagonal close-packed pattern was also considered as not being due to the inner one of the three nitride layers. It appeared more probable that this innermost layer has a face-centered cubic lattice, since it shows a twinned structure and the presence of this crystal structure was indicated in the X-ray spectrograms. The indications are, therefore, that the hexagonal close-packed pattern was due to the intermediate one of the three nitride layers.

TABLE 2.—*Results of X-ray examination of various electrolytic iron and steel specimens nitrided at different temperatures*

[E. I.=Electrolytic iron. Steel=Al-Mo nitriding steel (2.5 per cent Al; 0.85 per cent Mo; 0.25 per cent C.)]

Nitrided specimen			Nitriding treatment		Crystal structure of nitrided case, as determined by X rays [2]	Lattice parameter a_0 [3] (A. U.)	Any face-centered cubic structure containing nitrogen present [4]
Laboratory No.[1]	Base material	Form—	°C.	Hours			
35	E. I.	Block	500	50	H. c. p.; B. c. c.	H. c. p.=2.72; B. c. c.=2.86.	No.
77	do	do	500	50	H. c. p.	H. c. p.=2.72	Yes (1).
10	do	do	500	75	H. c. p. (and B. c. c.)	H. c. p.=2.71	No.
166 T	Steel	do	500	50	H. c. p.	do	Yes (1).
166 B	do	do	500	50	do	do	Do.
E 2	E. I.	Powder	540	50	do	H. c. p.=2.706±0.004	Do.
1000	do	do	540	50	do	H. c. p.=2.715±0.006	No.
7	do	do	550	2	H. c. p. (and B. c. c.)	H. c. p.=2.708±0.006	Do.
E 3	Steel	Sheet, 0.017 inch thick.	540	50	H. c. p.	H. c. p.=2.71	Yes (3).
37	E. I.	Block	600	25	B. c. c.; H. c. p.	B. c. c.=2.86; H. c. p=2.73.	Yes (2).
168 T	Steel	do	600	25	H. c. p.	H. c. p.=2.71	Yes (3).
168 B	do	do	600	25	H. c. p.; B. c. c.	H. c. p.=2.71; B. c. c.=2.86.	Yes (1).
13	E. I.	Powder	650	[5] ½	B. c. c. (and F. c. c. (N)).	B. c. c.=2.856 (F. c. c. (N)=3.777).	Yes. (2).
9	do	do	650	[6] 4	F. c. c. (N); H. c. p. (?).	F. c. c., (N)=3.780±0.003.	Yes (5).
E 1	do	do	700	25	H. c. p.	H. c. p.=2.703±0.005	Yes (1).
39	do	Block	700	25	B. c. c.; F. c. c.	B. c. c.=2.86; F. c. c.=3.60	Yes (2).
170 T	Steel	do	700	25	B. c. c.; F. c. c. (and H. c. p.).	B. c. c.=2.86; F. c. c.=3.61.	Yes (1).
170 B	do	do	700	25	do	B. c. c.=2.85; F. c. c.=3.61.	Yes (2).
E 4	do	Sheet, 0.017 inch thick.	700	25	H. c. p.; B. c. c.	H. c. p.=2.70; B. c. c.=2.86.	Yes (2) or 3).

[1] The T and B after the three specimen numbers in this column stand for the top (decarburized before nitriding) and bottom (not decarburized) faces of the block specimens in question. (See text.)

[2] H. c. p.=hexagonal close-packed ($C=c_0/a_0=1.619$); B. c. c.=body-centered cubic (a_0 for pure alpha iron=2.855 A.); F. c. c.=face-centered cubic (a_0 for pure gamma iron=3.60 A). In the cases where more than one crystal structure is present the more pronounced one is placed first. The structure reported in parentheses was present only to a small extent. F. c. c. (N) is face-centered cubic structure which is assumed to contain nitrogen in its space lattice, having a lattice parameter of about 3.80 A. U.

[3] With reference to the block and sheet specimens, the bands in the diffraction patterns were, as a rule, not sharply defined, more so for the interplanar spacings ($d_{h,k,l}$), of less than about 1.2 A. U. where the bands were broad and ill-defined and in some cases overlapped. After the usual corrections had been made for any length changes in the film, the deviations of the observed values from the theoretical values were plotted and corrections based on mean deviations were applied to the observed values. The results so obtained are reported only to the second decimal place. These difficulties did not apply to the powder specimens, so the results for these specimens are reported to the third decimal place.

[4] The figures given in parentheses are the number of bands observed which would fit in with a face-centered cubic structure having a lattice parameter of about 3.80 A. U. (3.789 A. U. according to Hägg) and could be clearly distinguished from the bands belonging to the hexagonal close-packed structure. It was noted that the theoretical values for several of the interplanar spacings in both the hexagonal close-packed and nitrogen-bearing face-centered cubic structures coincided. Since the series of hexagonal close-packed structure bands was more complete, the bands at the coinciding points were generally assumed to be due to this structure, unless the band in question appeared to be more intense than should be expected and in such cases the joint presence of the hexagonal close-packed and face-centered cubic bands was assumed. It was also noted that the band in the nitrogen-bearing face-centered cubic structure, due to interplanar spacing=approximately 1.90 A. U. possessed, in general, a strong intensity while the other observed bands were of weak or very weak intensity.

[5] Annealed in nitrogen after nitriding.

[6] Not annealed in nitrogen after nitriding.

In the discussion of the tentative iron-nitrogen diagram, which follows, the intermediate layer has been assigned the composition Fe_4N. There is, therefore, disagreement with the results reported by Hägg [17] who, in X-ray analyses of nitrided pure iron obtained by reducing powdered iron oxide with hydrogen and nitriding the iron

[17] Hägg, G., X-ray Studies on the Nitrides of Iron, Nature, 121, p. 826; 1928.

in the usual way, has given evidence indicating that the compound Fe_4N is face-centered cubic. Results somewhat similar to those obtained by Hägg were reported by other investigators,[18] but the X-ray data available at present appear to be insufficient to decide the matter definitely. It should be noted that no doubt is cast on the result obtained by Hägg that the compound Fe_2N is hexagonal close packed, and it may, perhaps, be suggested, in view of the very marked increase in the lattice parameter of the hexagonal close-packed patterns shown by him between the specimens of 6.1 and 11.3 per cent nitrogen content and likewise noted by Osawa and Iwaizumi, that the compounds Fe_4N and Fe_2N both have hexagonal close-packed patterns, the latter having the greater parameter.

It seems probable that the discrepancies in interpretation of the X-ray data are more apparent than real. Since Fry's diagram, which has probably been used as the basis for interpretation, does not recognize the presence of Fe_6N, the inner nitride layer is presumably taken by other workers as Fe_4N. If Fe_6N is admitted to be present, the discrepancies lie in the interpretation, not in the observations. Here again, as in the thermal analysis, interpretation is difficult because of the heterogeneous nature of the specimens and of inablility to isolate one layer at a time for study.

Reference was made above to the presence of a face-centered cubic lattice, to which the innermost layer described in the microscopic examination and given the composition Fe_6N, in the tentative iron-nitrogen diagram (fig. 20) was assigned. This face-centered cubic lattice appears to have a parameter of about 3.80 A. U., which is in good agreement with that reported by Hägg (3.789 A. U.). There was also found present in specimens 39, 170 T and 170 B a face-centered cubic lattice having a parameter of about 3.60 A. U. similar to that for pure gamma iron. It is suggested that this last face-centered cubic lattice may be due to rapidly cooled Braunite, which was present in some of the specimens and might be expected to give a face-centered cubic pattern analogous to that of austenite in quenched-high carbon steel. It might be mentioned that, in addition to the lines ascribed to the foregoing lattices, a number of lines possessing a very weak intensity in all cases were met with in a number of the diffraction patterns. Their identity has not yet been established.

VI. TENTATIVE IRON-NITROGEN DIAGRAM

The tentative diagram which has been drawn as a result of the study described above is given in Figure 20. It is to be emphasized, that this diagram is not an "equilibrium" diagram, as the term is generally used. The iron-nitrogen alloys are unstable and equilibrium conditions can not be determined without taking account of the pressure of nitrogen in the system and the activity of the nitrogen; that is, whether it is atomic or nascent or molecular. For instance, the temperature of the point *D* in the diagram, showing the stability limit of the compound Fe_4N, which was determined upon heating in ammonia gas, would undoubtedly be considerably lower in vacuum. It was even suspected during the work that since the arrests during the

[18] Osawa, G., and Iwaizumi, S., X-ray Investigation of Iron-Nitrogen Alloys, Sci. Repts., Tohoku Imperial Univ., (Sendai, Japan), **18**, p. 79; 1929; Z. Krist, **69**, p. 26; 1928; Chem. Abst. **23**, p. 2408; 1929. Brill, R., The Crystal Lattice of Fe_4N., Z. Krist, **68**, p. 379; 1928; Chem. Abst., **23**, p. 2083; 1929.

thermal analyses were obtained on heating and not on cooling, most of the nitrogen being evolved during the run, they might be due entirely to decomposition and not to transformations between the solid constituents. Therefore a short series of tests were made. Seven samples of the nitrided granular electrolytic iron ranging in nitrogen content from 0.30 to 3.43 per cent were selected. The apparatus used consisted of an electric tube furnace through which was inserted a quartz tube, fitted to allow introduction of an alundum boat containing a weighed sample (2 g) and with connections to a vacuum pump and pressure gages. Temperature measurements were made by means of a portable potentiometer and 22 gage chromel-alumel thermocouple adjacent to the alundum boat containing the sample. Several blank runs were first made to determine the effect of heating upon the pressure variations of the evacuated system.

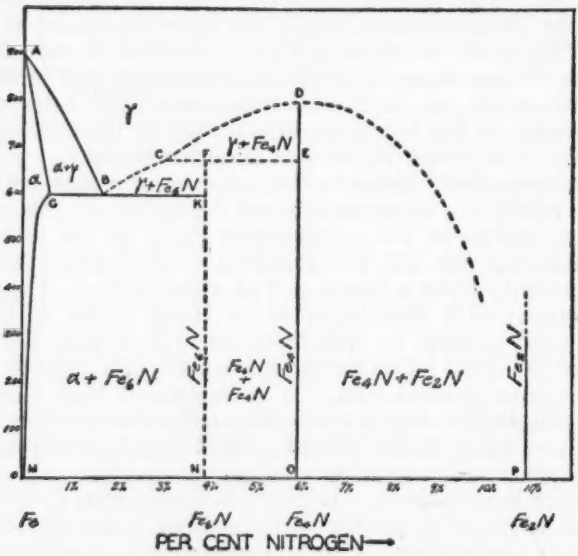

FIGURE 20.—*Tentative iron-nitrogen diagram*

Two pressure gages were used. A McLeod gage permitted pressure measurements up to 0.41 mm. Hg and an open end mercury manometer permitted readings of higher pressures.

One weighed sample of each nitrogen content was heated in the evacuated system for 15 minutes at 625° C. and another at 685° C., which are the temperatures corresponding approximately to the end of the two transformation ranges found by thermal analysis. A heating rate of approximately 7° C. per minute was maintained. Pressure readings were made at intervals of 50° C. and each 5 minutes of the 15 minutes at temperature. The specimens were cooled in the sealed system and then analyzed for residual nitrogen. Figure 21 shows the pressure variations during heating of some of the samples. The first noticeable increase in pressure due to evolution of gas occurred at 200° to 250° C. and another increase in pressure at 400° to 450° C., the magnitude of this latter increase being governed by the initial nitrogen content. Samples of higher nitrogen content gave the

greatest increase. As the temperature was raised to 625° or 685° C., the pressure increased rapidly. Considerably higher pressures were obtained upon heating to 685° C. than by heating to 625° C. All samples showed a loss of weight after heating and in every case the samples heated to 685° C. showed a greater loss than the corresponding sample heated to 625° C. Chemical analysis of the samples for residual nitrogen confirmed the weight losses. Since evolution of gas began well below the temperatures of the transformation ranges and the pressures increased continuously and not in two sudden stages, it seems that the heat effects at the two transformation temperatures can not be attributed solely to decomposition. They really represent phase changes.

That the thermal arrests represented transformations between the solid constituents was, of course, confirmed by the microscopic examination. It may also be mentioned that, since the nitrided specimens were prepared by diffusion and not by melting, the composition gradients are not smooth but occur in steps between adjacent nitrided layers. As called for by the principles underlying the construction of equilibrium diagrams, a duplex field marked $Fe_8N + Fe_4N$ has been indicated in the diagram; actually there were no signs of such a field in the microstructure. The compounds were found to occur directly adjacent to each other. A similar result obtained in the diffusion of melted zinc into solid copper at 450° C. has been described by Hudson.[19]

The outer, intermediate, and inner layers noted in the microstructure have been designated as the compounds Fe_2N, Fe_4N, and Fe_8N, respectively. (Fig. 20.) No chemical analyses of the compositions of the individual nitride layers were made, as they could not be sharply separated, and stoichiometric relations such as those of Noyes and Smith, [20] who reported Fe_2N, Fe_4N, Fe_6N, and Fe_8N as possible compounds, were used as the principal guide for setting the compositions of the layers. This construction is a modification of Fry's diagram, which showed only two layers. The intermediate layer described in the microscopic examination is the one which corresponds in microstructure to Fry's Nitride I, and it should be noted Fry designated this layer as Fe_2N whereas in this diagram it is designated Fe_4N.

This departure from Fry's diagram appears to be justified by the fact that the outermost layer was not noted by Fry and because the construction shown fits in with the thermal analysis data obtained by Sawyer and in this work. Moreover, on the grounds of Fry's own observations it would appear better to designate his Nitride I (corresponding with the intermediate layer described in this study) as Fe_4N, instead of Fe_2N. The layer, Nitride I, in Fry's micrographs is shown to be stable at the nitriding temperature of 680° C, which he used, whereas his diagram indicates the compound Fe_2N to be unstable at comparatively low temperatures.

Since the outermost layer, designated as Fe_2N, has a 2-phase eutectoid-like structure it may be considered as a eutectoid between the compounds Fe_4N and Fe_2N, the eutectoid transformation probably occurring below 425° C., as indicated by Figure 10 (*f*) in which the

[19] Hudson, O. F., The Critical Point at 460° C. in Zinc Copper Alloys, J. Inst. Metals, **12**, No. 2, p. 89; 1914.

[20] Noyes, A. A., and Smith, L. B., The Dissociation Pressure of Iron-Nitrides, J. Am. Chem. Soc., **43**, No. 1, p. 475; 1921.

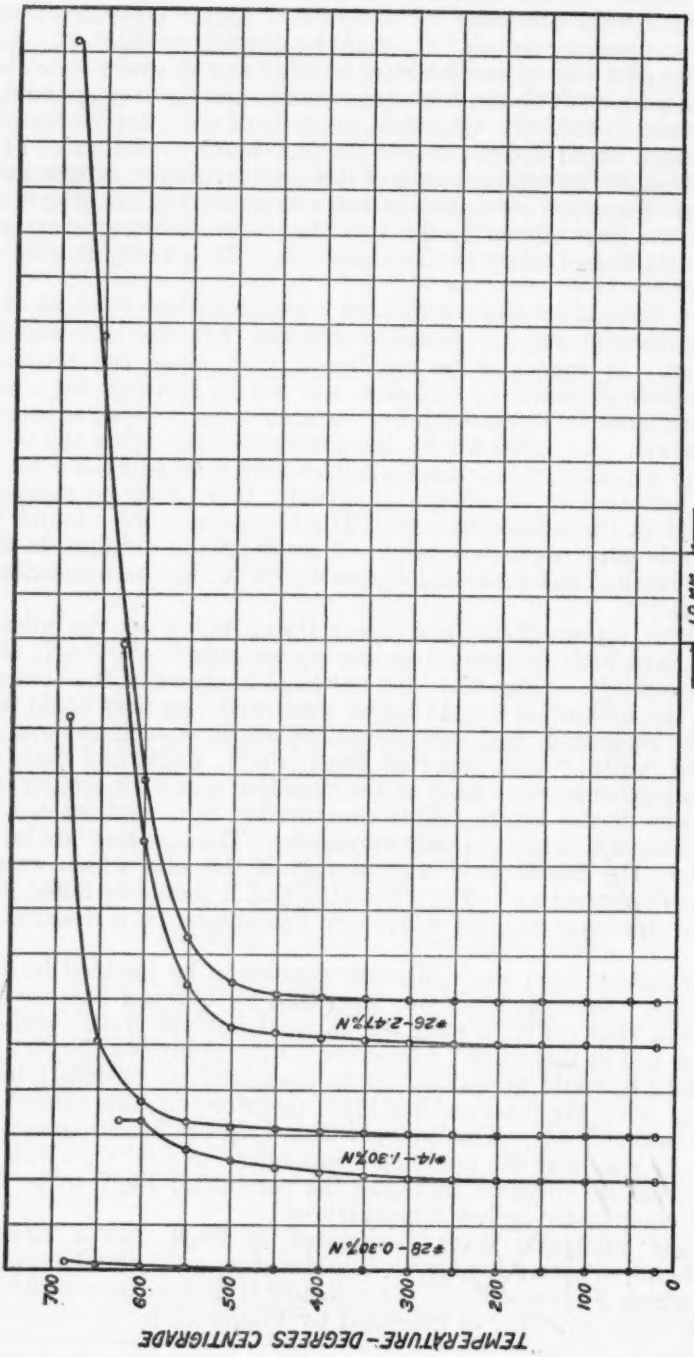

FIGURE 21.—*Change of pressure during the heating of some of the samples for thermal analysis*

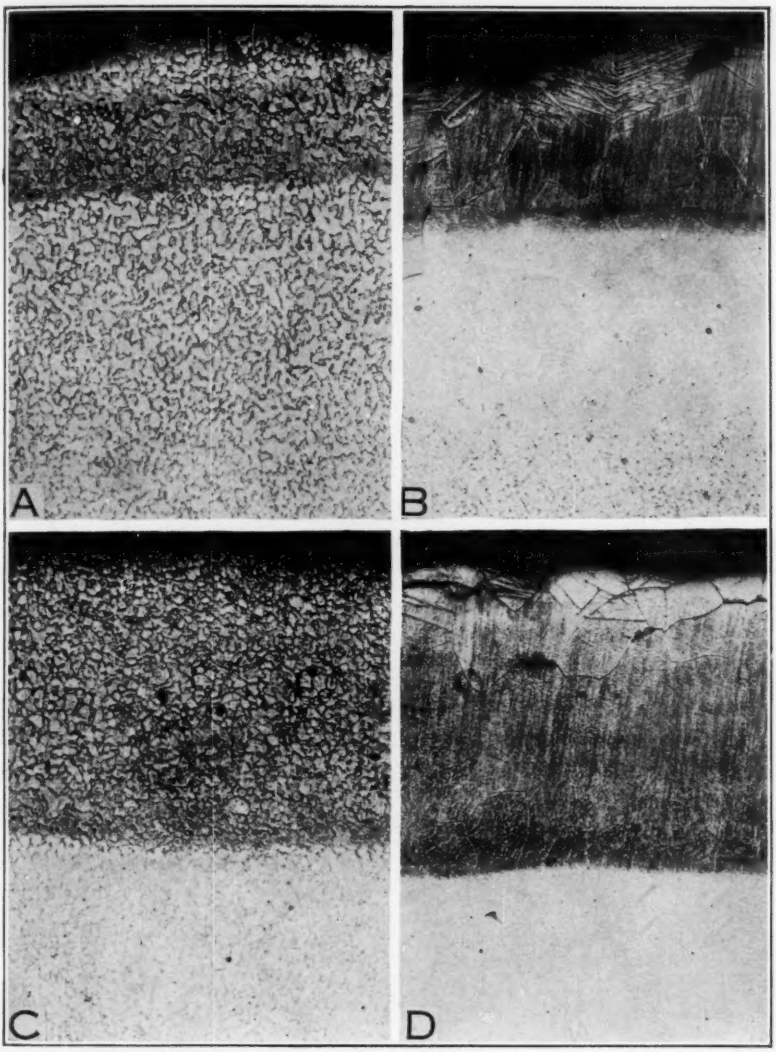

FIGURE 22.—*Nitrided layers in special aluminum-molybdenum nitriding steels,* × *100*

a, Nitrided 50 hours at 500° C. Note that the original structure of the steel can still be discerned in the nitrided layer. There is only one layer. No nitride needles were detected in the cores of any of the nitrided steels; *b*, same as specimen *a*, but at edge decarburized before nitriding. Note the coarse crystal structure and the wide slip lines or twins near the surface; *c*, nitrided 25 hours at 600° C. The nitrided layer is deeper than in *a* or *b* because of the higher temperature of nitriding; *d*, same as specimen *c*, but at decarburized edge. Slip lines are present in the coarse crystals, but they are not so numerous as in *b*, nitrided at the lower temperature.

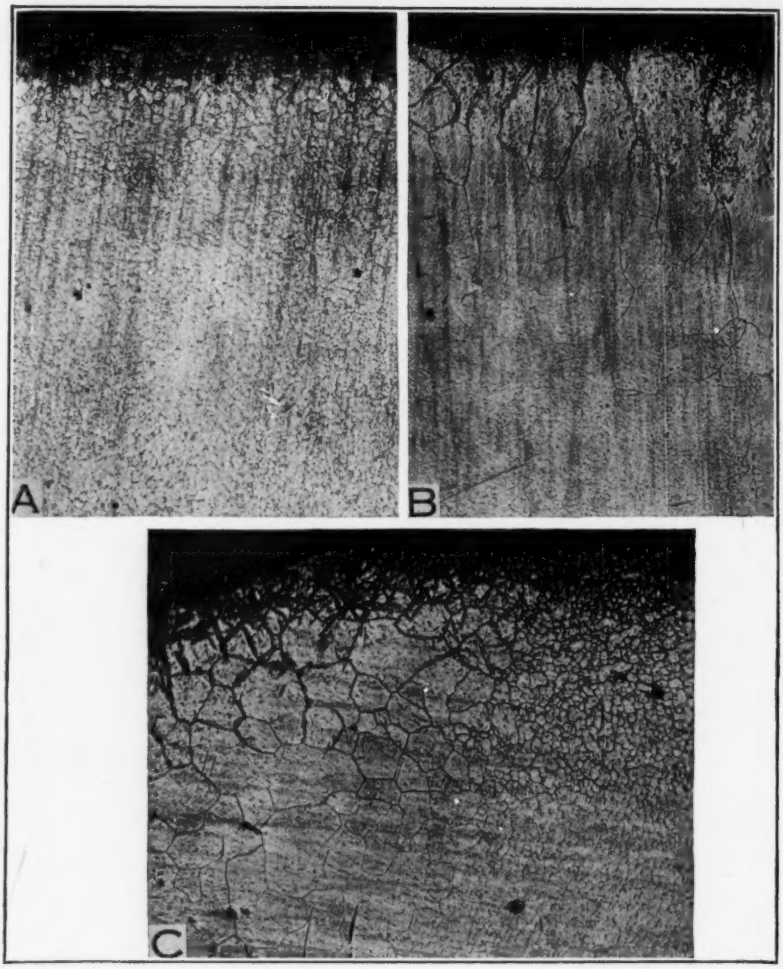

FIGURE 23.—*Structure of steel specimens nitrided 25 hours at 700° C., × 100*

a, Fine grain at undecarburized edge of block; *b*, coarse grain at decarburized edge of block. At this high nitriding temperature, however, no slip lines appeared; *c*, juncture of decarburized and undecarburized edge. Note the intergranular darker constituent which appears at this nitriding temperature.

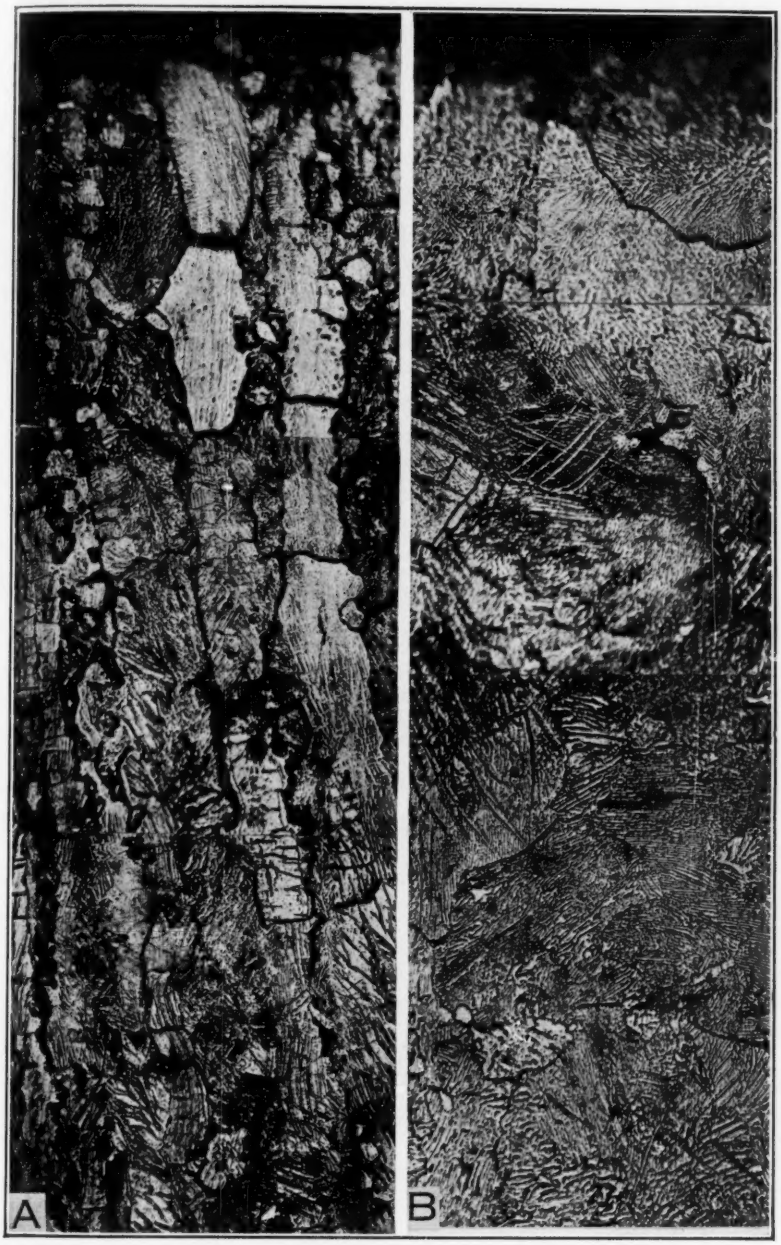

FIGURE 24.—*Slip lines in nitrided layers,* × *500*

Nitrided 25 hours at 540° C. *a*, Note number of slip or check lines toward the interior. These slip lines were found to be present very close to the core; *b*, this specimen contained no molybdenum.

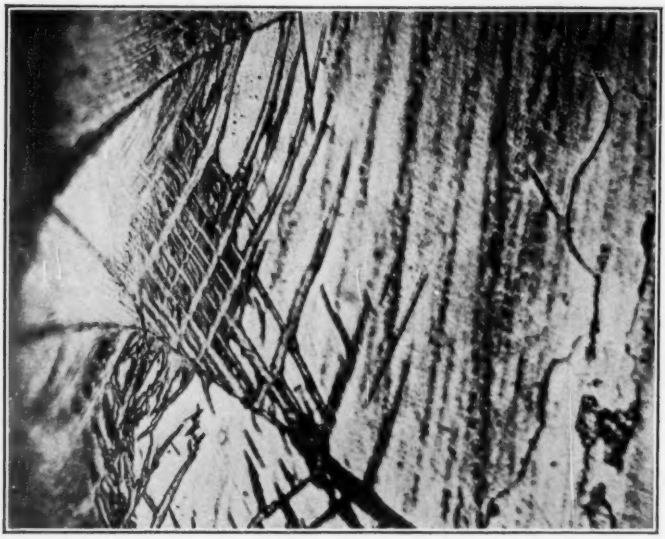

FIGURE 25.—*Slightly rounded twins and slip lines in coarse-grained nitrided layer,* × *500*

Nitrided 25 hours at 540° C. at the decarburized edge of the block.

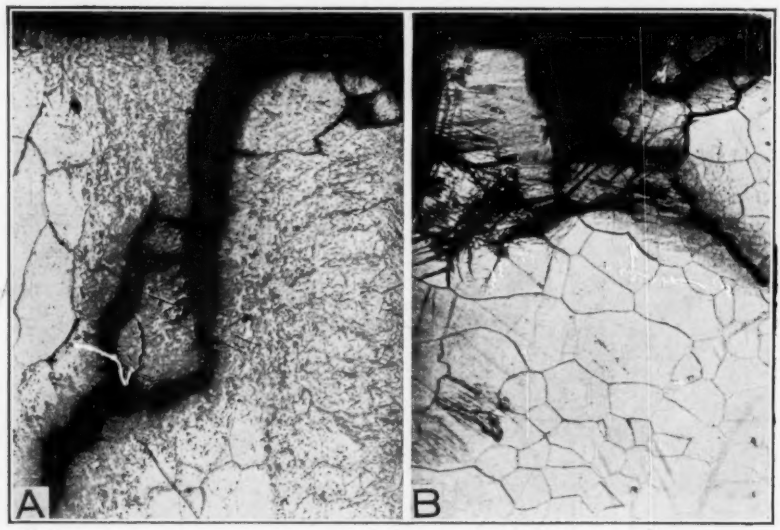

FIGURE 26.—*Fissures and darker etching constituent in nitrided specimen heated to 725° C. in* NH_3, ×*500*

a, Nitrided 25 hours at 600° C., then heated one hour in NH_3 at 725° C.; *b*, nitrided 25 hours at 700° C., then heated one hour in NH_3 at 725° C.

eutectoid structure was obtained by nitriding at that temperature. There was, however, no indication of such a eutectoid shown by the thermal analysis.

From the results of Noyes and Smith the innermost layer might have been designated either Fe_6N or Fe_8N, since they consider both are possible. However, a vertical line corresponding to the compound Fe_8N of approximately 3 per cent nitrogen content meets the upper horizontal at the point *C*, in which case the lines *BC*, *CD*, and *CE*, would all meet the vertical line of the compound at the point *C*. This does not appear at all probable and the compound Fe_6N was chosen to designate the innermost layer.

The reasons for modifying Fry's and Sawyer's diagrams by the peritectoid horizontal *CE* have already been given. For the solid solubility line *MG* Fry's diagram has been followed, although it appears that the solid solubility at the eutectoid temperature, namely, the point *G*, is not very definitely established. The temperatures for the lower eutectoid horizontal *GK*, 600° C., and the upper peritectoid horizontal *CE*, 675° C., are taken as rounded figures, from the results of Sawyer, Fry, and those obtained in this study.

Fry's temperature scale has been regarded as about 10° too low [21] and this was considered in setting the temperature of the eutectoid horizontal at 600° C. It will be noted that the point *C* at 3 per cent nitrogen content, at which composition the upper horizontal begins, is at a considerably higher nitrogen content than the composition at which the upper horizontal first appeared in the thermal analyses. As shown in Figure 5 this was at 1.25 per cent. As has already been stated, however, the nitrogen content in the nitrided layers in this composition range appeared to be about three times the average nitrogen content. The location of the point *C* for the beginning of the upper horizontal is therefore in fair agreement with the thermal analysis results.

Since in the present work the peritectoid transformation was completed below 675° C. in a large majority of the cases and always began below 660° C., it is possible that the rounded value of 675° C. is a trifle high.

VII. OBSERVATIONS ON THE STRUCTURE OF NITRIDING STEELS

The aluminum-molybdenum nitriding steels mentioned in connection with the X-ray analyses were also examined under the microscope. They contained 2.5 per cent aluminum, 0.85 per cent molybdenum, and carbon 0.25, except one specimen (see fig. 24) which contained 0.50 per cent carbon and no molybdenum. As may be seen in Figure 22, the steel specimens, unlike the nitrided iron specimens, showed only one nitrided layer, which was yellowish in color darkened brown by etching with picric acid. The original structure of the steels was not changed to any degree by the nitriding and may be discerned in the nitrided layer. (Fig. 22 (*a*)). Even in specimens of nitrided sheet of this material, the original worked structure still remained, the nitriding being evident in the microstructure only by the yellowish tinge of the nitrided layer. In none of the steel speci-

[21] Bramley, A., and Haywood, F. W., Determination of the Iron-Iron-Nitride Eutectoid, Carnegie Schol. Mem., 17, p. 76; 1928.

mens, including those which were heated to 725° C. was there any evidence of a eutectoid layer corresponding to Braunite. The steel specimens also differed from the nitrided iron specimens in that in the former no nitride needles were present in the case, which is, of course, important on account of the embrittling effect of the nitride needles. The absence of nitride needles in the nitriding steels is most readily explained by the fact that only one nitrided layer is present. As was pointed out by Fry and observed in the microscopic examination of the nitrided iron specimens, the familiar nitride needles are evidently due to the innermost layer, which is not formed in these special alloy steels used for commercial nitriding.

The steel specimens were nitrided at 500°, 600°, and 700° C., respectively. Those nitrided at the lower temperatures appeared to be more brittle than those nitrided at the higher temperatures. The specimens were in the form of blocks, one edge of which had been decarburized before nitriding. In these decarburized edges of the specimen the grain size was comparatively large and in the specimens nitrided at the lower temperatures these large-grained areas showed profuse twinning and slip line formation, as shown in Figures 22 (*b*) and (*d*) and in Figure 25. In the specimens nitrided at the higher temperatures, however, the slip lines did not appear to any marked degree, as shown in Figure 23 (*b*) and (*c*). Moreover, in the fine-grained areas slip lines or twins were practically absent even in those nitrided at the lower temperatures, as shown in Figures 22 (*a*) and (*c*). Since the slip lines which formed in the large grained areas are evidently an indication of brittleness it is apparent that the presence of surface decarburization in nitriding steel should be guarded against. Due to the extreme hardness of the nitrided layer, particularly at the surface, it would be expected to be very brittle. It was observed, as shown in Figure 24, in specimens in which the nitrided layer was tapered off gradually by grinding, that large numbers of slip or check lines were also present very close to the core. This is especially apparent in the specimen shown in Figure 24 (*a*).

Two of the specimens were heated to 725° C. in ammonia for one hour. After this treatment, as shown in Figure 26, the nitrided layers gave evidence of the presence of another constituent which was etched slightly darker than the matrix by sodium picrate. Fissuring of a type probably similar to that described by Vanick, Sveshnikoff, and Thompson [22] also occurred. These authors concluded that fissuring was generally preceded by decarburization.

It was observed that the fissuring of these specimens was also much more pronounced in the edges of the specimens which had become decarburized before nitriding.

In the X-ray analyses summarized in Table 2 the steel specimens nitrided at 700° C. showed more than one crystal pattern, whereas those nitrided at the lower temperatures showed only one pattern, namely, the hexagonal close packed. Under the microscope also, as shown in Figure 23, another constituent was noticed, present as a grain boundary network. This result is of some interest, since nitrided articles have been suggested for use at comparatively high temperatures, and it would appear necessary to obtain assurance of the stability of the different nitriding steels at these temperatures.

[22] Vanick, J. S., Sveshnikoff, W. W., and Thompson, J. G., Deterioration of Steel in the Synthesis of Ammonia, B. S., Tech. Paper No. 361.

VIII. SUMMARY

1. In a study of the iron-nitrogen system, thermal analyses, microscopic examinations, and X-ray analyses were made of nitrided electrolytic iron specimens. From the data obtained and, with the diagrams of Sawyer and Fry as a basis, a modified iron-nitrogen constitution diagram has been tentatively drawn.

2. The thermal analysis data, in general, confirm those of Sawyer which indicated that there are two temperature horizontals on the high nitrogen side of the diagram, but the microscopic examination indicated that the upper horizontal represented a peritectoid reaction, and not a eutectoid transformation as Sawyer supposed.

3. Three iron nitride layers were observed, whereas Fry in his pioneer work and Murakami in his recent work noted two. The outer, intermediate, and inner layers have been designated as Fe_2N, Fe_4N, and Fe_6N, respectively.

4. In X-ray analyses a hexagonal close-packed pattern and indications of a face-centered cubic pattern were obtained. According to the microstructure of the layers it appeared probable that the face-centered cubic lattice was due to the inner layer Fe_6N and the hexagonal close-packed pattern to the intermediate layer Fe_4N; this is not in agreement with the interpretation of X-ray data by Hägg, Osawa, and other investigators who ascribe the face-centered cubic lines to Fe_4N. The data available at present do not appear to be sufficient to definitely decide the matter.

5. Observations on several nitrided specimens of aluminum molybdenum nitriding steel were also made. Those nitrided at the usual nitriding temperatures contained only one layer and showed a hexagonal close-packed pattern.

ACKNOWLEDGMENT

The authors wish to express their indebtedness to H. O. Willier for his conscientious and very efficient aid in the nitriding and the metallographic examination of the large number of specimens necessary in the latter phases of the investigation. The Fixed Nitrogen Laboratory cooperated in the work by furnishing the very pure ammonia required.

WASHINGTON, June 21, 1929.

MELTING, MECHANICAL WORKING, AND SOME PHYSICAL PROPERTIES OF RHODIUM

By Wm. H. Swanger

ABSTRACT

In continuation of the work on the platinum metals a method for the purification, and the technic for the melting and mechanical working of rhodium have been developed. New determinations of a number of the physical constants of rhodium have been made on the specially purified material.

The melting point of rhodium has been determined as 1,985° C. ± 10°. The metal can be melted with an oxyhydrogen flame on a block of hard-burned lime or in vacuum by means of the high-frequency induction furnace, using fused thoria crucibles.

The metal as melted is not malleable at room temperature, but can be readily forged at temperatures above 800° C. It has been hot swaged to wires of 1 mm diameter. These wires, swaged above 800° C. are not ductile, and have a coarse-grained, equiaxed structure. By continuing the working of the wire at gradually decreasing temperatures, a fibrous structure is imparted to the wire and it becomes ductile and can be drawn at room temperature.

New determinations of physical properties of rhodium gave the following results: Density, 12.4 − g/cm³; length of side of unit cube (face centered) of the rhodium lattice, $a_o = 3.77$ A; electrical resistivity, 4.93 microhm-centimeters at 20° C.; thermal emf. against platinum at 1,200° C., 18.42 mv; temperature coefficient of resistance, 0° to 100° C., 0.00436; average coefficient of thermal expansion 20° to 50° C., 9.6×10^{-6}; hardness (baby Brinell 12.8 kg load, 1/16-inch ball) 101. The reflecting power is constant across the visible spectrum, but drops off rapidly in the ultra-violet.

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I. INTRODUCTION

The work done in the past few years at the Bureau of Standards on methods for the purification of the platinum metals has made available very pure material for determining the properties of these metals and of their alloys. The present paper will outline the work

which has been done on the melting, the mechanical working, and the physical properties of pure rhodium.

Although rhodium has been known since 1804, when it was discovered by Wollaston, its use has been limited almost entirely to the platinum-rhodium alloys for thermocouples, which contain 10 or 13 per cent of rhodium. The lack of its application to other uses has been chiefly due to its scarcity. Crude platinum, its chief source of supply, contains only about 1 per cent of rhodium. According to statistics of the Bureau of Mines,[1] the stock of rhodium (plus ruthenium and osmium) in the hands of refiners at the end of the year 1927 was 4,369 ounces compared to 68,000 ounces of platinum, and the imports of rhodium into the United States during the year were 1,308 ounces compared to 128,000 ounces of platinum.

Aside from its scarcity, the difficulties in fabrication have probably kept pure rhodium from the list of industrially useful metals. Mention of specimens of mechanically worked rhodium occurs in a few places in the literature, but no description is given as to the methods used, other than that the specimens were prepared only with great difficulty.

II. PREPARATION OF RHODIUM SPONGE

The pure rhodium sponge used in the present work for the preparation of rods and wires of rhodium was prepared by the method described by Wichers, Gilchrist, and Swanger.[2] Briefly this process consisted of heating commercial or crude rhodium, in finely divided form, with sodium chloride in an atmosphere of chlorine gas, to a temperature of about 600° C. The partially fused mass of sodium rhodium chloride thus obtained was dissolved in water. This solution was then boiled with an excess of sodium nitrite, which converted the rhodium to the soluble sodium rhodium nitrite. A small amount of sodium sulphide was then added to remove lead as sulphide. Some of the platinum and palladium present was also precipitated, but not much of the rhodium. After filtration, a saturated solution of ammonium chloride was added to precipitate ammonium rhodium nitrite $(NH_4)_3\,Rh(NO_2)_6$. This salt was easily decomposed by hydrochloric acid, yielding a solution of rhodium chloride. The foregoing process was then repeated as many times as necessary to produce a final product of the desired degree of purity.

As ammonium rhodium nitrite is not a suitable salt for reduction to sponge by ignition, it was converted to ammonium rhodium chloride. This salt was ignited in air, and the somewhat oxidized sponge thus obtained was reduced in hydrogen.

Preparations of rhodium sponge made by this process have shown no impurities by spectrographic examination, except for traces of iridium in some instances. The melts described in the present paper were made from these preparations.

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[1] Platinum and Allied Metals in 1927, Jewelers Circular, **96**, No. 19, p. 55; 1928.

[2] E. Wichers, R. Gilchrist, and Wm. H. Swanger, Purification of the Six Platinum Metals, Trans. A. I. M. E., **76**, pp. 602-630; 1928.

III. MELTING AND WORKING OF RHODIUM

1. MELTING IN THE OXYHYDROGEN FLAME

The first melts of pure rhodium were made with a "hard" (oxygen rich) oxyhydrogen flame, the rhodium being held on a block of hard-burned lime. It was found desirable to press the rhodium sponge into pellets in a steel mold before melting.

As soon as the rhodium melts in the oxyhydrogen flame it begins to spit, small beads of metal are thrown off very rapidly, and when the melt freezes large excrescences form on the surface. This is presumably due to the evolution of gases which have been absorbed from the flame by the molten metal.

By sufficiently reducing the flow of oxygen to the melting torch, this spitting of rhodium can be avoided to a considerable extent and the metal made to freeze with a fairly smooth surface. It is, of course, realized that a flame of this type—that is, a soft flame rich in hydrogen—may reduce lime at the temperature of molten rhodium, and introduce calcium into the melt. However, by proper manipulation of the flame, only the upper portion of the metal is melted at any one time, and the liquid metal can be kept out of contact with the lime while exposed to this soft flame. A button of rhodium melted in this manner can be lifted from the lime block cleanly with no adherence of lime to the metal.

2. MELTING IN THE HIGH-FREQUENCY INDUCTION FURNACE

The melting of rhodium sponge in the high-frequency induction furnace with access of air presents somewhat the same difficulties as does melting on lime with the oxyhydrogen flame. The sponge must be compressed to a density sufficient to heat readily from the induced current. If the pellets are heated in air to a bright red and then allowed to cool to room temperature, the sponge will be oxidized to such a degree that it can not be heated readily in the high-frequency furnace. By heating and cooling in hydrogen such oxidized rhodium sponge can be reduced to clean metal which will then heat easily in the induction coil.

Molten rhodium in an open crucible in the induction furnace spits badly, and if the furnace current is shut off suddenly, so that the metal freezes rapidly, large blisters will grow out from the surface. By proper manipulation of the furnace current the metal can be frozen slowly so that a minimum of blistering occurs, and forgeable ingots are obtained.

The first melts in the induction furnace were made in zirconium oxide crucibles similar to those used at the bureau for the melting of pure platinum.[3] However, it was found that this refractory softened at the temperatures sometimes attained in the molten rhodium. Nevertheless, it broke away cleanly from the frozen metal and with care could be used for the melting of rhodium. One attempt to cast the molten rhodium into a graphite mold was unsuccessful, as most of the metal was ejected from the mold by the rapid evolution of gas on sudden freezing.

[3] L. Jordan, A. A. Peterson, and L. H. Phelps, Refractories for Melting Pure Metals: Iron, Nickel, Platinum, Trans. Am. Electro-chem. Soc., **50**, p. 162; 1926.

A single melt of rhodium was made in an Acheson graphite crucible to confirm the reported solution of carbon by molten rhodium. There was no spitting or sprouting of the metal on freezing. The button was very hard and brittle and could not be forged either hot or cold. The increase in weight of the metal by melting in graphite was 1.8 per cent. The color of the metal was noticeably darker than that of pure rhodium.

Thorium oxide crucibles were found the most satisfactory for melting pure rhodium in the procedure finally adopted; that is, melting in vacuum in the high-frequency induction furnace. For the preparation of these crucibles pure thorium oxide was fused in the electric arc in a stream of oxygen according to the method described by Fairchild and Peters.[4] The fused thoria was ground in a steel-ball mill, using steel balls, and was then treated with hydrochloric acid to remove iron. The acid-washed fused oxide was mixed with a small amount of thorium chloride solution, and this mixture was pressed or tamped in suitable molds designed to form a crucible with a wall thickness of about 3 mm. The molded crucibles were dried and then fired to 1,700° to 1,800° C. in an Arsem furnace. Care had to be taken in this firing to avoid direct contact between thoria and graphite at temperatures much above 1,200° C. Thoria crucibles prepared in this manner are very dense and possess considerable strength. They have been used to melt platinum metal alloys at temperatures up to 2,200° C.

The melting of rhodium in vacuum in the high-frequency furnace will be described in more detail under the discussion of the melting point of rhodium. It is sufficient for the present to state that melts in vacuum were made in thoria crucibles at a pressure of 0.5 to 1.0 mm of mercury. Rhodium melted under these conditions froze with a smooth surface of a silver-white color. Ingots of the maximum density reported for rhodium have been obtained in this way.

3. FORGING AND SWAGING

The vacuum melts of rhodium weighed usually about 50 g each. They were made in thoria crucibles measuring about 22 mm in diameter at the top, 12 mm at the bottom, and 30 mm deep (all inside dimensions). These melts were allowed to freeze in the crucibles. The ingots were about 20 mm long. The shrinkage cavity generally extended over so large a portion of the length of these small ingots that satisfactory forgings could not be made from them.

Several vacuum-fused ingots broke up when forging was attempted. The crystals of these ingots were very large—up to 5 or 6 mm across—and the fractures appeared to be intercrystalline. On the other hand, a number of ingots prepared in apparently the same way from the same lot of rhodium sponge and having just as large crystals were forgeable. It has not yet been found possible to control the forgeability of the vacuum-fused metal.

Vacuum-melted ingots remelted on lime with the oxyhydrogen flame, however, always proved forgeable and this procedure was followed in preparing rods and wire. The forging or swaging of the remelted rhodium ingots did not present any unusual difficulties.

[4] C. O. Fairchild and M. F. Peters, U. S. Patent No. 1545951; July 14, 1925.

These ingots could not be forged at room temperature, but became quite malleable above a red heat.

For the production of wire the ingots were hand forged at about 1,100° C. to bars of a shape and size (diameter of 10 mm) suitable for swaging. The bars were heated in an oxygas or oxyhydrogen flame and entered the swaging dies at about 1,000° C. A rotary swager operating at 400 r. p. m. was used for bars from 10 to 1.8 mm in diameter. A smaller machine, operating at 600 r. p. m., was used for further swaging to 1.0 mm. Although dies were available for this machine to produce wire of 0.8 mm diameter, it was found that the machine would not pass the wire through fast enough to prevent its cooling below the temperature at which it was malleable. Consequently the hot swaging of rhodium wire of any considerable length was not carried to sizes below 1.0 mm.

A piece of 1 mm wire about 35 feet long was prepared by hot swaging to be used as a winding for a resistance furnace in a study of certain reactions at temperatures higher than could be obtained in a platinum-wound furnace. This wire was wound on a grooved alundum tube 1.5 inches in diameter with six turns per linear inch. It was heated to a red heat with a gas flame as it was wound on the tube. The furnace has been kept at a temperature of 1,875° C. for four hours, although it is not intended to be used regularly at temperatures quite this high.

At the present time data are not available on the rate of deterioration of rhodium wire due to volatilization when used at high temperatures. When rhodium is heated to relatively low temperatures in air it becomes covered with an oxide film which disappears when the temperature reaches about 1,200° C. If it is quenched in water or dilute hydrochloric acid from above this temperature it remains bright with a silvery white luster.

4. DRAWING OF RHODIUM WIRE

The rhodium wire produced by swaging at 800° C. or over was not ductile at room temperature. It could not be straightened out from a sharp bend without fracturing, nor reduced in diameter by cold-drawing. The fracture appeared coarsely crystalline. The end of a piece of such wire could be flattened on an anvil to half its thickness by one sharp blow with a hammer, but fractured when the same thing was attempted with several light blows.

It was thought that if a fibrous structure could be imparted to the hot-swaged wire it might become ductile. In view of the results obtained in the hot-drawing of rhodium this probably could be accomplished during swaging by gradually lowering the temperature of the wire as it is passed through the successively smaller dies until finally it might be swaged at a temperature considerably below a red heat or cold-drawn at room temperature. However, there was not enough material available for much experimental work along this line.

Recently, through the courtesy of Dr. S. L. Hoyt, of the General Electric Research Laboratory, a set of tungsten carbide wire drawing dies, covering the range 0.41 to 0.020 inch, was made available to the bureau. These dies can be used at a red heat. A piece of wire which had been hot-swaged to a diameter of 1 mm was successfully drawn

through this series of dies to approximately 0.5 mm (0.020 inch) in diameter. The dies were kept at about 600° C. by means of a gas burner. The wire was heated somewhat hotter (600° to 800° C.) as it passed through the die for the first three or four steps in reduction, but the temperature of the wire was gradually lowered until, for the last three or four dies, the wire was well below a red heat. The wire was lubricated by dipping it into a suspension of fine graphite in oil before each pass through the die. After this hot drawing operation the wire, now 0.020 inch in diameter, was drawn through a set of jewel dies at room temperature, without any annealing, to 0.0144 inch. The resulting wire was ductile and could be bent sharply and straightened, coiled on an 8-inch rod, and twisted tightly upon itself without breaking, all at room temperature. It is quite probable that drawing at room temperature could be continued to wire of still smaller size. It is thus demonstrated that rhodium which has heretofore generally been reported as unworkable can be made ductile.

The microstructure of a longitudinal section of wire swaged to 0.040 inch diameter at a temperature above 800° C. is shown in Figure 1. The microstructure of a longitudinal section of a piece of the swaged wire after it was drawn to 0.014 inch diameter, as described in the preceding paragraph, is shown in Figure 2.

The change from the relatively coarse-grained equiaxed structure of the swaged wire to the distinctly fibrous structure of the ductile wire is clearly seen.

5. MELTING POINT OF RHODIUM

One of the most useful applications of rhodium wire appeared to be for windings for high-temperature furnaces or heaters. Rhodium has a melting point considerably higher than platinum and like platinum does not readily oxidize or volatilize in air at high temperatures. In this connection it seemed advisable to redetermine the melting point of rhodium. The figures generally given in the literature for the melting point of rhodium, namely, 1,950° or 1,955° C., were based on determinations made on metal which was probably not of the highest purity.

With the collaboration of H. T. Wensel, W. F. Roeser, and F. R. Caldwell, of the pyrometry section of the bureau, a number of determinations of the melting point of rhodium were made. An Ajax-Northrup high-frequency induction furnace was used for melting the rhodium. The arrangement is shown in Figure 3. The metal was melted in a thoria crucible, *A*, within a closed-end fused silica tube, *D*, which was evacuated. For heat insulation, ignited, but not fused, powdered thorium oxide, *C*, was packed about the crucible. An alundum extraction thimble, *B*, was used to hold the heat insulation and crucible inside the silica tube. The top of the silica tube was closed with the clear fused-silica cover plate, *E*, whose absorption correction had been determined. The melting was carried out at pressures below 1 mm of mercury, with a liquid-air trap between the mechanical vacuum pump and the melting chamber. Temperature measurements were made with a Leeds & Northrup optical pyrometer sighted into a 2 mm hole drilled in the ingot to a depth of 10 to 15 mm.

The pyrometer was calibrated in the bureau's pyrometry section, and in addition was checked at the gold point and at the melting point

FIGURE 1.—*Rh. wire swaged to 0.040 inch diameter at a temperature above 800° C. × 100. Etched with fused $KHSO_4$*

FIGURE 2.—*Rh. wire drawn from 0.040 to 0.020 inch diameter at temperatures between 700° and 400° C. and from 0.020 to 0.014 inch diameter at room temperature. × 100. Etched with fused $KHSO_4$*

of platinum using the same high-frequency furnace set-up that was used for determining the melting point of rhodium.

The temperatures corresponding to the melting points were determined both by plotting time-temperature heating curves and by observing the temperature at which the hole in the ingot filled with liquid metal. The flat portion of the heating curve for each melt extended over a period of at least two minutes during which time about 10 readings were taken. In all satisfactory experiments the last temperature reading obtained before the hole in the ingot filled was the same as the temperature corresponding to the flat portion of the heating curve. In some cases the sight hole had not been drilled deep enough into the ingot and the reflection of the cold top portion of the evacuated tube from the bottom of the hole appeared as a dark spot in the center of the image of the hole. This caused an error in that the values obtained for the brightness in the hole were obviously too low. The ratio of the depth of the sight hole to the diameter should be at least 8 to 1.

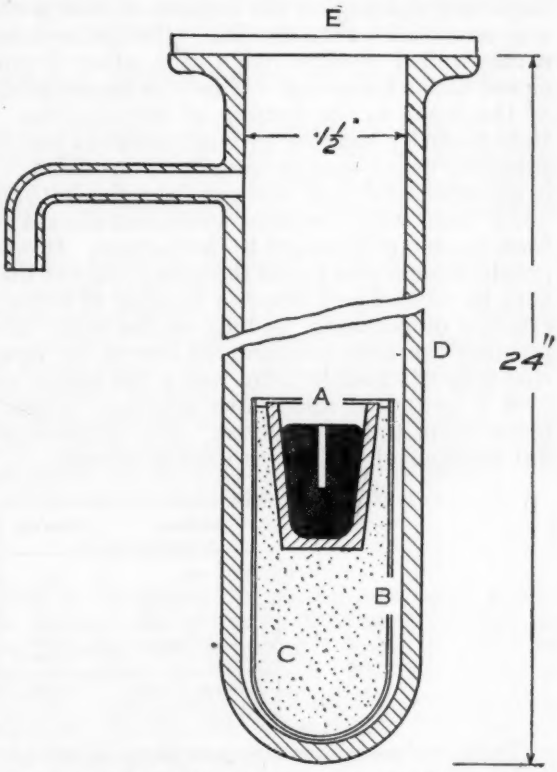

FIGURE 3.—*Vacuum furnace assembly for melting rhodium by high-frequency induction*

Cooling curves could not be taken as satisfactorily as heating curves. In all cases, however, it was possible to obtain two or three constant readings on the liquid surface of the melt while solid metal was spreading over the surface from the sides of the crucible. The correction necessary to convert the apparent temperature obtained by sighting on the freezing liquid surface of rhodium to true temperature was approximated by comparing the brightness in the hole and on the solid surface of several rhodium ingots just below the melting point. The difference in brightness thus obtained was used for correcting the apparent temperature of the liquid surface at the freezing point. This correction is somewhat too large, since the emissivity of liquid rhodium has been found to be slightly higher than that of solid rhodium, and, consequently, the values obtained for the freezing point are presumably somewhat higher than the true value.

77886°—29——14

On two separate ingots, with the best black body conditions in the sight holes, the values for the melting point were 1,986° and 1,987° C., respectively. The values for the freezing points from the same two experiments were 2,006° and 2,002° C., respectively.

Another series of observations was made [5] on a third ingot, using a precision optical pyrometer [6] to make the temperature measurements. An arrangement of furnace, evacuated tube, and crucible similar to that described above was used, except that a "black body" was obtained somewhat differently. Instead of drilling a hole in the ingot and sighting on the bottom of that, a cover (of thorium oxide) was cemented on the crucible. To the bottom of this cover was fixed a thin-walled thorium oxide tube, about 2 mm inside diameter, and closed at the lower end. The tube projected down through the center of the ingot to the bottom of the crucible. Temperature readings were made by sighting through a hole in the cover into the reentrant tube into which enough loose thorium oxide that had been poured to fill it about one-third of the way from the bottom. This gave a "black body" into which to sight which was about two-thirds of the distance from the top of the ingot to the bottom. It is considered that the temperature measured inside the tube is that of the metal. The metal can thus be melted and frozen a number of times without disturbing the crucible or contents, as long as the sight tube remains intact. On plotting the time-temperature curves for determinations made with this type of crucible there was a flat region on each curve extending over a period of about five minutes. Observations were made on three melts and five freezes. The temperatures corresponding to the flat portions of the curves were as follows:

Melting	Freezing
° C.	° C.
1,985	1,984
1,984	1,985
1,984	1,983
	1,986
	1,983
Average... 1,984	1,984

These values show the precision to which the brightness at the melting and freezing points of rhodium can be determined, but does not necessarily mean that the conversion of these measures of brightness to degrees centigrade was as accurate as the agreement between the separate determinations. Up to the present time accurate checking of the factors entering into this conversion has not been made. The temperatures given above are certainly accurate to within ±10°. The pyrometry section of the bureau, within whose province the accurate determinations of melting points come, is planning to make a more precise determination of the melting point of rhodium in the near future, and the uncertainty of the temperature conversion will then be much less than 10° C.

From the results of the two methods described, the melting point of rhodium is given tentatively as 1,985° C. ± 10°.

[5] Observations by H. T. Wensel, W. F. Roeser, and F. R. Caldwell.
[6] C. O. Fairchild, W. H. Hoover, and M. F. Peters, A New Determination of the Melting Point of Palladium, B. S. Jour. Research, 2 (RP65); May, 1929.

Most of the tables of physical constants of the elements give the melting point of rhodium as 1,950° or 1,955° C. Mendenhall and Ingersoll [7] determined the melting point of rhodium based on the melting points of gold as 1,065° C. and of platinum as either 1,745° or 1,789° C. Their value was 1,907° C. (Pt = 1,745° C.) or 1,968° C. (Pt = 1,789° C.). Von Wartenberg [8] reported his own determinations of the melting point of rhodium as 1,940° C. based on $C_2 = 1.460$ cm degrees and recalculated a previous determination by Holborn and Henning to 1,946° C. These two values become approximately 1,970° and 1,975° C., respectively, on the International Temperature Scale, which is based on the value 1.432 cm degrees for C_2.[9]

IV. OTHER PHYSICAL PROPERTIES OF RHODIUM

In the course of the experiments on the melting and working of rhodium, as suitable specimens became available for the determination of physical constants they were submitted to the laboratories of the bureau most directly concerned with the particular measurements required.

New determinations of the following physical constants were made by the members of the bureau staff named below: Density by Miss E. E. Hill, X-ray lattice constant by E. C. Groesbeck, electrical resistivity by A. R. Lindberg, thermal electromotive force and temperature coefficient of resistance by F. R. Caldwell, thermal expansion by W. T. Sweeney, and reflecting power by W. W. Coblentz and R. Stair. Grateful acknowledgment is made for this assistance in obtaining new data on the properties of rhodium. A number of hardness determinations made by the author are also included.

A short description of the above determinations follows:

1. DENSITY

Previous determinations of the density of rhodium reported in the literature range from 11.0, the value given by Wollaston in 1804, to 12.6 (g/cm^3). Holburn, Austin, and Henning [10] found a value of 12.44 for rhodium foil prepared by Heraeus. The most recent determinations are by Rose.[11] He found 12.22 for the density of an ingot which was forged from sponge but not melted. The density of another ingot, melted and forged, was 12.47. In reviewing previous determinations Rose calculated that the value 12.6 given by Mylius and Dietz [12] would become 12.51 when corrected for the impurities, chiefly iridium, which the rhodium contained. He further states that the density of pure rhodium, melted and forged, might be provisionally taken as 12.5

In the present work the density of three rhodium ingots after melting in vacuum was 12.42, 12.41, and 12.41 g/cm^3, respectively. The three ingots were then melted together on a block of lime with

[7] C. E. Mendenhall and L. R. Ingersoll, The Melting Points of Rhodium and Iridium, Phys. Rev., **25**, pp. 1–16; 1907.

[8] H. von Wartenberg, Über optische Temperaturmessung blanker Körper, Verhandl. deut. physik. Ges., **12**, pp. 121–127; 1910.

[9] "C_2" is the constant in Wien's radiation law which, together with the value of 1,063° C. for the melting point of gold, defines the high temperature scale.

[10] L. Holborn, F. Henning, L. Austin, Die Zerstäubung und Recristallisation Elektrisch Geglühter Platinmetalle, Wiss. ab. Phys. Tech. Reichsanstalt, **4**, p. 87; 1903.

[11] Sir Thomas Kirke Rose, On the Density of Rhodium, Jr. Inst. Metals, **33**, No. 1, pp. 109–110; 1925.

[12] F. Mylius and R. Dietz, Reine Platin-Metalle im Handel, Ber., **31**, p. 3189, 1899.

an oxyhydrogen flame. The button was hot forged and then hot swaged to a rod 7 inches long by 0.265 inch in diameter. The density of this rod was 12.40 g/cm^3. The rod was subsequently hot swaged to 0.040-inch wire. The density of the wire was also 12.40 g/cm^3.

2. X-RAY DIFFRACTION DATA

The crystal lattice of rhodium is face centered cubic. Hull [13] determined the length of the side of the unit cube, a_o to be 3.82 Angstroms. Barth and Lunde [14] have more recently given $a_o = 3.794$A. If a_o is taken as 3.82 the calculated density of rhodium is 12.16 which is quite certainly lower than the true density. The calculated density becomes 12.43 if $a_o = 3.794$, a value nearer to the observed density.

Two determinations of the length of the side of the unit cube made on the rhodium sponge used in the present work gave:

First determination $-a_o = 3.773 \pm 0.0025$ A
Second determination $-a_o = 3.774 \pm 0.002$ A

The density calculated from these values is 12.6, which is somewhat higher than the observed density. However, it is generally agreed that the density calculated from the value for the lattice constant is always higher than the density obtained by direct determination.

3. ELECTRICAL RESISTIVITY

The resistivity of pure rhodium as determined on wire hot swaged to a diameter of 1 mm and annealed at a temperature well over 1,200° C. was 4.93 microhm-centimeters at 20° C.

The value given in the International Critical Tables is 5.1 at 20° C. In Carter's [15] tabulation of the physical properties of rhodium the resistivity at 0° C. is given as 5.11.

4. THERMAL ELECTROMOTIVE FORCE AGAINST PLATINUM

The thermal electromotive force of rhodium against the bureau's purest platinum (Pt. standard No. 27) was determined for temperatures of the hot junction from 0° C. to 1,100° C. with the cold junction at 0° C. The results are given in Table 1.

TABLE 1.—*Thermal electromotive force of rhodium against platinum*

Temperature	Emf.	Temperature	Emf.	Temperature	Emf.
° C.	mv	° C.	mv	° C.	mv
0	0.00	500	5.28	900	12.04
100	.70	600	6.77	1,000	14.05
200	1.61	700	8.40	1,100	16.18
300	2.68	800	10.16	1,200	*18.42
400	3.92				

* Extrapolated.

[13] A. W. Hull, X-Ray Crystal Analysis of Thirteen Common Metals, Phys. Rev., **17**, pp. 571–588; 1921.
[14] T. Barth and G. Lunde, Der Einfluss der Lanthanidenkontraction usw, Zeit Phys. Chem., **117**, pp. 478–490; 1925.
[15] F. E. Carter, The Platinum Metals and Their Alloys, A. I. M. E., Proc. Inst. Metals Div. p. 759; 1928

5. TEMPERATURE COEFFICIENT OF ELECTRICAL RESISTANCE

At the time this determination was made wire less than 1 mm in diameter was not available. The resistance of this wire was too low to make a measurement of the change of resistance with change of temperature with reasonable accuracy. To provide a suitable specimen, about 1 m of the wire was clamped between electrical leads and a current passed through the wire to heat it to dull redness. The hot wire was passed back and forth between the rolls of a small hand rolling mill until a ribbon 0.007 inch thick was obtained. This ribbon was fairly ductile. The resistance was measured at 0° and at 100° C. The average temperature coefficient of resistance between these temperatures was 0.00436. Holborn [16] reported a value of 0.00443. Additional determinations of this important physical constant will be made.

6. THERMAL EXPANSION

The linear coefficient of thermal expansion of rhodium was determined by the interferometric method. The values given in Table 2 are considered accurate to within 1 per cent.

TABLE 2. *Thermal expansion of rhodium*

Temperature range	Average coefficient of expansion per degree centigrade
° *C.*	$\times 10^{-6}$
20 to 50	8.1
20 to 100	8.3
20 to 200	8.5
20 to 300	8.9
20 to 400	9.3
20 to 500	9.6

The International Critical Tables give the coefficient of thermal expansion as 8.4×10^{-6} at 20° C. Carter, in his tabulation of the physical properties of the platinum metals, gives 8.4×10^{-6} at 20° C. and 8.5×10^{-6} at 40° C.

7. REFLECTING POWER

A determination was made of the reflecting power of rhodium in the visible and in the ultra-violet spectrum to wave length 250 mμ. The surface of the ingot that was used did not have a good polish and diffused considerable radiation. Instead of having a reflecting power of 78 per cent in the visible spectrum as previously determined by Coblentz [17] it was only about 45 per cent. However, the reflecting power was fairly constant across the visible spectrum, but dropped off rapidly in the ultra-violet until at 250 mμ it was about two-thirds of the value in the visible spectrum.

[16] L. Holborn, Uber die Abhängigkeit des Widerstandes reiner Metalle von der Temperatur, Ann. d. Physik. (4), 59, p. 145; 1919.
[17] W. W. Coblentz, The Reflecting Power of Various Metals, B. S. Sci. Paper No. 152.

8. HARDNESS

Hardness determinations were made on several specimens of the melted and forged rhodium. The shape of the specimens as melted made it impracticable to make hardness determinations without forging, although a Brinell number was obtained on the ingot as melted. The hot-forged specimens were annealed at a temperature well over 1,200° C. The following values were obtained:

TABLE 3.—*Hardness of rhodium*

	Specimen A melted but not forged	Specimen B melted and forged	Specimen C melted and forged
Baby Brinell 12.5 kg, ½-inch ball	101	101	
Rockwell "L" 100 kg, ¼-inch ball		90	85
Scleroscope		12	19
Vickers hardness tester, 136° diamond pyramid 10 kg		121	125
Herbert pendulum (fine hardness)		16.4	19

Carter [10] has given the baby Brinell hardness of cast rhodium as 139.

The hardness values obtained in the present work correspond quite closely with those of hard-rolled copper. Despite this apparent softness, rhodium does not machine readily. Great difficulty was experienced in drilling the sight holes in the specimens used for melting-point determinations. An ordinary twist drill made hardly any impression. Flat drills made of carbon-steel drill rod quenched from bright red heat in ordinary zinc chloride soldering flux seemed to give the best results.

V. ACKNOWLEDGMENT

Grateful acknowledgment is made to Louis Jordan, of the metallurgy division, whose aid and advice contributed materially to the accomplishment of the work reported in this paper.

WASHINGTON, August 2, 1929.

[10] See footnote 10, p. 1038.

OPTICAL ROTATION AND RING STRUCTURE IN THE SUGAR GROUP

THE OPTICAL ROTATION OF THE VARIOUS ASYMMETRIC CARBON ATOMS IN THE HEXOSE AND PENTOSE SUGARS

By H. S. Isbell

ABSTRACT

The specific rotations of α-*d*-guiose (+61.6), α-methyl *d*-guloside (+106) and β-methyl *d*-guloside (−83), which are reported for the first time, complete the data necessary for the calculation of the optical rotatory power of each of the various asymmetric carbon atoms in the hexose sugars. The values for the optical rotatory power of the various asymmetric carbon atoms in both the hexose and pentose series are calculated first, from the optical rotations of the methyl glycosides, and, secondly, from the optical rotations of the sugars. The values from the glycosides are slightly higher, but of the same order as the values obtained from the sugars indicating that the normal forms of *d*-glucose, *d*-galactose, α-*d*-mannose and α-*d*-gulose have the same ring structure as the corresponding glycosides (1, 5). The slightly larger values for the glycosides indicates that the replacement of the hydroxyl group in the sugars by a methoxy group alters the rotation of all the asymmetric carbon atoms. The utilization of the values given is illustrated by the explanation of certain deviations from Hudson's second rule of isorotation and the prediction of the optical rotations of the at present unknown hexose sugars and methyl glycosides.

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I. INTRODUCTION

In 1875 van't Hoff formulated the rule of optical superposition and illustrated it quite plainly in its application to the carbohydrate field.[1] This rule states the optical rotation of the molecule is the algebraic sum of the constituent asymmetric carbon atoms, the

[1] Voir Chimie dans l'Espace, van't Hoff, Rotterdam, 1875.

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Hardness determinations were made on several specimens of the melted and forged rhodium. The shape of the specimens as melted made it impracticable to make hardness determinations without forging, although a Brinell number was obtained on the ingot as melted. The hot-forged specimens were annealed at a temperature well over 1,200° C. The following values were obtained:

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Baby Brinell 12.8 kg, 1/16-inch ball	101	101	----------
Rockwell "E" 100 kg, 1/8-inch ball	----------	90	85
Scleroscope	----------	12	10
Vickers hardness tester, 136° diamond pyramid 10 kg	----------	121	125
Herbert pendulum (time hardness)	----------	16.4	15

Carter [18] has given the baby Brinell hardness of cast rhodium as 139.

The hardness values obtained in the present work correspond quite closely with those of hard-rolled copper. Despite this apparent softness, rhodium does not machine readily. Great difficulty was experienced in drilling the sight holes in the specimens used for melting-point determinations. An ordinary twist drill made hardly any impression. Flat drills made of carbon-steel drill rod quenched from a bright red heat in ordinary zinc chloride soldering flux seemed to give the best results.

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[18] See footnote 15, p. 1038.

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The specific rotations of α-*d*-gulose (+61.6), α-methyl *d*-guloside (+106) and β-methyl *d*-guloside (−83), which are reported for the first time, complete the data necessary for the calculation of the optical rotatory power of each of the various asymmetric carbon atoms in the hexose sugars. The values for the optical rotatory power of the various asymmetric carbon atoms in both the hexose and pentose series are calculated first, from the optical rotations of the methyl glycosides, and, secondly, from the optical rotations of the sugars. The values from the glycosides are slightly higher, but of the same order as the values obtained from the sugars indicating that the normal forms of *d*-glucose, *d*-galactose, α-*d*-mannose and α-*d*-gulose have the same ring structure as the corresponding glycosides (1, 5). The slightly larger values for the glycosides indicates that the replacement of the hydroxyl group in the sugars by a methoxy group alters the rotation of all the asymmetric carbon atoms. The utilization of the values given is illustrated by the explanation of certain deviations from Hudson's second rule of isorotation and the prediction of the optical rotations of the at present unknown hexose sugars and methyl glycosides.

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I. INTRODUCTION

In 1875 van't Hoff[1] formulated the rule of optical superposition and illustrated it quite plainly in its application to the carbohydrate field. This rule states the optical rotation of the molecule is the algebraic sum of the constituent asymmetric carbon atoms, the

[1] La Chimie dans L'Espace, van't Hoff, Rotterdam; 1875.

rotations of the individual atoms changing from $+a$ to $-a$ when the atomic configuration is replaced by its mirror image. Van't Hoff illustrated this rule quite plainly in its application to the carbohydrate field as will be discussed below. However, at that time the experimental data were lacking to establish its validity in the sugar group. In 1909 the development of experimental carbohydrate chemistry was sufficient for Hudson[2] to apply the superposition rule by his method of considering only the rotations of the first asymmetric carbon and the rest of the molecule and to determine the optical rotation of the first carbon atom and the rotation of the rest of the molecule. He compared all kinds of derivatives by his method and by this way of comparison showed that the principle of optical superposition holds approximately. In order to make comparisons between substances whose structure differs considerably he made a number of rules ("isorotation") or approximations. The correlation of rotation in the sugar group by him and others showed that there exist many deviations[3] from his rules, which indicate that the influence of a given group on the rotatory power of the various asymmetric carbon atoms is manifested throughout the sugar molecule.

A test of the theory of optical superposition was anticipated by van't Hoff[4] in 1894, who states that when there are several asymmetric carbon atoms their action is to be added or subtracted. "Thus for the four pentose types COH $(CHOH)_3$, we should have the following rotations:

No. 1	No. 2	No. 3	No. 4
+A +B +C	+A +B −C	+A −B +C	−A +B +C

and since the sum of No. 2, No. 3, and No. 4 is equal to A+B+C, the rotation of arabinose (probably the highest) should be equal to the rotations of xylose, ribose, and the expected fourth type taken together." [5]

Van't Hoff's idea may be put in the form of four simultaneous equations which contain only three variables, and if the experimental values of A, B, and C, determined from any three of the equations check the fourth equation, his theory as applied in the given case is definitely proved. If one had a similar series of compounds, which checked, it would be strong evidence that all the compounds in the series had similar structures. The realization of the experimental proof of this reasoning has not been possible because of the lack of knowledge and sufficient experimental data. The problem is far more complicated than van't Hoff could anticipate at that early date. However, in the light of modern knowledge upon the ring structure of the sugars it should now be possible to reach the desired goal if the necessary data were available.

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[2] Hudson, J. Am. Chem. Soc., **31**, p. 69; 1909.
[3] Böeseken, The Configuration of the Saccharides, A. W. Sijthoff's, Leyden.
[4] Van't Hoff, The Arrangement of Atoms in Space (translated by Eiloart), Longmans, Green & Co., p. 160; 1898.
[5] Discovered since, and called lyxose.

The author is attempting to prepare those compounds necessary for the calculation and *checking* of the optical rotatory power of all the different asymmetric carbon atoms in the hexose sugars and methyl glycosides. The investigation, which is still in progress, has been successful, in that the optical rotations of α-*d*-gulose and α- and β-methyl *d*-gulosides have been determined. These values complete the data necessary for the computation of the optical rotation of each of the several asymmetric carbon atoms in the hexose sugars and in the methyl glycosides. The values obtained for the rotatory power of the different asymmetric carbon atoms are of particular interest because they are the primary values from which the optical rotation of all the normal aldohexose sugars and methyl glycosides may be calculated. The numerical values for the at present unknown normal forms of *d*-idose, *d*-talose, *d*-allose, and *d*-a[illegible]se and the corresponding methyl glycosides are predicted. An attempt is being made to prepare and measure the optical rotation of one or more forms of *d*-idose. If the optical rotations which may be found in the future check the predicted values, it will be strong evidence that all the sugars involved in the calculations have similar ring structures.

1. DETERMINATION OF RING STRUCTURE BY THE AGREEMENT WITH OR DEVIATION FROM THE THEORY OF OPTICAL SUPERPOSITION

At the time when van't Hoff first presented the theory of optical superposition the reducing sugars were considered to be true aldehydes. Subsequently it has been found that the sugars and glycosides exist in two isomeric forms (α and β) which contain an additional asymmetric carbon atom. In 1883 Tollens [6] had suggested a ring structure for the reducing sugars, but discovery of the two methyl glycosides by Emil Fischer [7] in 1893 marks the beginning of the modern concept of the structure of the sugars. The optical rotation of the pseudo-aldehydic carbon atom was determined in 1909 by C. S. Hudson, who by a series [8] of brilliant researches has developed the theory of optical superposition into the most useful tool at the disposal of sugar chemists. Hudson [9] has considered the rotation of the pseudo-aldehydic carbon as $+a$ in the alpha (dextro) sugars, $-a$ in the beta sugars, and the rotation of the rest of the molecules as b. The rotation of the α-*d*-form is equal to $b+a$ and the rotation of the β-*d*-form is equal to $b-a$. He has shown from the available data, first, that the difference between the molecular rotations of the α and β forms of all the aldehyde sugars and their derivatives ($2a$) is a nearly constant quantity, and, secondly, that the α and β forms of those derivatives of any aldose sugar in which only the first carbon is affected have molecular rotations whose sum is approximately equal to the sum ($2b$) of the molecular rotations of the α and β forms of the sugar. Certain exceptions were found to the above rules, particularly in the mannose, rhamnose, and lyxose series, which led to

[6] Tollens, Ber., **16**, p. 921; 1883.
[7] Fischer, Ber., **26**, p. 2400; 1893.
[8] Hudson, Relations Between Rotatory Power and Structure in the Sugar Group, B. S. Sci. Paper No. 533.
[9] See footnote 2, p. 1042.

the hypothesis[10] "that among the known derivatives of mannose and rhamnose there occur substances of various ring types (which accounts for the observed exceptional comparative rotations) and that substances belonging to the same ring type show normal comparative rotations (which accounts for the normal values)." The hypothesis and allocation of the various substances to the different series which he postulated was vigorously attacked by Haworth and Hirst.[11] They regard α- and β-mannose as being not necessarily dissimilar in ring structure and believe that the divergence in optical rotation may be caused by the special arrangement of hydroxyl groups in mannose and the related sugars rhamnose and lyxose. In their studies they found a new form of lyxose whose rotation (-70) is also exceptional. However, Hudson's hypothesis has recently received additional support in the preparation by Dale[12] of a calcium chloride double compound of a new form of α-*d*-mannose whose rotation agrees with the rotation calculated by Hudson for a certain ring form of β-*d*-mannose.

A comparison of the optical rotations of the sugars and glycosides only indicates that a given series of compounds have or have not a common ring form. The ring structure of said series is assumed to be the same as the ring structure of any substance in the series whose ring structure is established by other methods. The ring structures of these key substances are derived from the results obtained by methylation studies.

2. DETERMINATION OF RING STRUCTURE OF THE GLYCOSIDES FROM METHYLATION STUDIES

In 1903 Purdie and Irvine[13] showed that the hydroxyl groups in methyl glucoside could be replaced by methoxyl groups by means of methyl iodide and silver oxide. Since all the hydroxyl groups in the resulting pentamethyl glucose are blocked the ring structure is assumed to be fixed. The normal isomeric α and β pentamethyl glucoses, when hydrolyzed by acids, are converted into tetramethyl glucoses. Both of the tetramethyl glucoses exhibit mutarotation and give the same final rotatory power which shows that α and β tetramethyl glucose have the same ring structure. Recently Wolfrom and Lewis[14] have shown that tetramethyl glucose may be transformed by dilute alkalies directly to tetramethyl mannose, which shows that tetramethyl mannose and tetramethyl glucose have similar ring structures. Direct evidence on the location of the ring may be obtained by the oxidation of the methylated sugars to the corresponding sugar acids. Charlton, Haworth and Peat[15] found that those lactones prepared from the normal forms of glucose, galactose, mannose, arabinose, and xylose, by first methylating the aldoses and then submitting them to oxidation with bromine water, exhibited a rapid change in rotation when dissolved in water. This rapid change[16] indicates that 1,5 lactones were formed. This conclusion

[10] Hudson, J. Am. Chem. Soc., **48**, p. 1434, 1926.
[11] Haworth and Hirst, J. Chem. Soc., p. 1221; 1928.
[12] J. K. Dale, B. S. Jour. Research, **3**, p. 459; 1929; J. Am. Chem. Soc., **51**, p. 2788; 1929.
[13] Purdie and Irvine, J. Chem. Soc., **83**, p. 1021; 1903; **85**, p. 1049; 1904.
[14] Wolfrom and Lewis, J. Am. Chem. Soc., **50**, p. 837; 1928.
[15] Charlton, Haworth and Peat, J. Chem. Soc., p. 89; January, 1926.
[16] Levene and Simms, J. Biol. Chem., **65**, p. 31; 1925.

has been confirmed by the degradation of the various methylated sugar acids by nitric acid oxidation to the expected products. Thus tetramethyl gluconic acid prepared from the normal tetramethyl glucose on nitric acid oxidation gave a 70 per cent yield of xylotrimethoxyglutaric acid,[17] which indicates that the methylated sugar has a 1,5 ring structure.

The formation of the third methyl glucoside (the distillable so-called γ-form of Fischer [18]) and other similar compounds indicates that in a sugar solution an equilibrium [19] may exist between a number of different ring forms. As pointed out by Phelps and Purves the ring structure of a methylated sugar which might be prepared from such a solution would not determine the ring structure of the original sugar. When substitution is on the pseudo-aldehydic carbon atom as in the glycosides, the oxygen ring is more stable and probably it does not migrate upon further methylation. Hence, it may be assumed that the correct ring structure of glycosides is obtained from methylation studies, but that the ring structures of the sugars are not established by methylation.

It has been shown by methylation studies that α- and β-methyl glucosides,[20] α- and β-methyl galactosides,[21] α-methyl mannoside,[22] α- and β-methyl arabinosides,[23] α- and β-methyl xylosides,[24] and α-methyl lyxoside [25] have a 1, 5-ring structure. The only glycosides whose rotations were used and which have not been shown by methylation studies to have a 1, 5-ring structure are the author's newly prepared α- and β-methyl gulosides.[26] In this article it has been assumed that their ring structure is the same as the ring structure of the other crystalline glycosides.

The ring structures of the sugars were allocated by means of the concept that there occur different ring forms in the sugar group which may be detected by the wide deviation from Hudson's rules of isorotation. The rotation of each sugar was compared with the rotation of the corresponding glycoside by means of the following equations:

$$[M]_D \text{ (glycoside)} = B' \pm 18{,}500.$$

$$[M]_D \text{ (sugar)} = B \pm 8{,}500.$$

If the values of B and B' agree approximately it is assumed that the two substances have similar ring structures. The only exceptions as previously found by Hudson were in the mannose and lyxose series. A comparison of the numerical values shows that B ($-3{,}100$) from α-*d*-mannose ($+30$) agrees with the value of B' ($-3{,}170$) from α-methyl *d*-mannoside ($+79$) and hence it is assumed

[17] Haworth, Hirst and Miller, J. Chem. Soc., p. 2436; 1927.
[18] Fischer, Ber., **47,** p. 1980; 1914.
[19] Phelps and Purves, B. S. Jour. Research, **3,** p. 247; 1929; J. Am. Chem. Soc., **51,** p. 2443; 1929.
[20] Haworth, Hirst, and Miller, J. Chem. Soc., p. 2436; 1927.
[21] Haworth, Ruell, and Westgarth, J. Chem. Soc., **125,** p. 2468; 1924; Pryde, J. Chem. Soc., **123,** p. 1808; 1923.
[22] Goodyear and Haworth, J. Chem. Soc., p. 3136; 1927.
[23] Haworth, Hirst, and Learner, J. Chem. Soc., p. 2432; 1927.
[24] Hirst and Purves, J. Chem. Soc., **123,** p. 1352; 1923; Phelps and Purves, J. Am. Chem. Soc., **51,** p. 2443; 1929; also B. S. Jour. Research, **3,** p. 247; 1929.
[25] Hirst and Smith, J. Chem. Soc., p. 3147; 1928.
[26] It is planned to methylate the two methyl gulosides and determine their probable ring structure. The calculations are published at this time because it will be some time before the methylation studies are completed.

that they belong to the same series. The value of B (+5,440) from β-*d*-mannose (−17) does not check the value from the methyl glycoside (−3,170) which indicates that it has a different ring structure and it is therefore excluded from the calculations. The value of B (−2,000) from β-*d*-lyxose (−70) does not check the value of B' (−8,760) from α-methyl *d*-lyxoside and so it is also excluded from the calculations. The values of B and B' as well as the data used in the calculations are given in Table 1.

TABLE 1.—*Optical rotation of the aldose sugars and glycosides*

	$[\alpha]_D^{20}$ in H_2O	$[M]_D^{20}$	$[M]_D^{20}$ ±8,500 = B	$[M]_D^{20}$ ±18,500 = B	Ring from methylation	Ring assigned
α-*d*-glucose [1]	+113	+20,340	+11,840			1,5
β-*d*-glucose [1]	+19	+3,420	+11,920			1,5
α-methyl *d*-glucoside [2]	+157.9	+30,630		+12,130	1,5	1,5
β-methyl *d*-glucoside [2]	−32.5	−6,300		+12,200	1,5	1,5
α-*d*-mannose [3]	+30	+5,400	−3,100			1,5
β-*d*-mannose [3]	−17	−3,060	+5,440			
β-*d*-mannose (Dale's) [4]	−65	−11,700	−3,200			1,5
α-methyl *d*-mannoside [5]	+79	+15,330		−3,170	1,5	1,5
α-*d*-galactose [1]	+144	+25,920	+17,420			1,5
β-*d*-galactose [1]	+52	+9,360	+17,860			1,5
α-methyl *d*-galactoside [2]	+192.7	+37,380		+18,880	1,5	1,5
β-methyl *d*-galactoside [2]	−0.4	−80		+18,580	1,5	1,5
α-*d*-gulose [6]	+62.6	+11,100	+2,600			1,5
α-methyl *d*-guloside [6]	+106	+20,600		+2,100		1,5
β-methyl *d*-guloside [6]	−83	−16,100		+2,400		1,5
β-*d*-arabinose [1]	−175	−26,250	−17,750			1,5
β-*l*-arabinose [7]	+175	+26,250	+17,750			1,5
α-methyl *l*-arabinoside [1]	+17.3	+2,840		+21,340	1,5	1,5
β- methyl *l*-arabinoside [1]	+245.5	+40,260		+21,760	1,5	1,5
α-*d*-Xylose [1]	+92	+13,800	+5,300			1,5
α-methyl *d*-xyloside [1]	+153.9	+25,240		+6,740	1,5	1,5
β-methyl *d*-xyloside [1]	−65.5	−10,740		+7,760	1,5	1,5
α-*d*-lyxose [1]	+5.5	+825	−7,625			1,5
β-*d*-lyxose [8]	−70	−10,500	−2,000			
α-methyl *d*-lyxoside [9]	+59.4	+9,740		−8,760	1,5	1,5

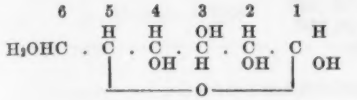
[1] B. S. Sci. Paper No. 533.
[2] Bourquelot, Ann. Chim., **7**, p. 218; 1917.
[3] Levene and Meyer, J. Biol. Chem., **57**, p. 329; 1923; **59**, p. 129; 1924.
[4] Dale, J. Amer. Chem. Soc., **51**, p. 2788; 1929.
[5] Van Ekenstein, Rec. trav. chim., **15**, p. 223; 1896.
[6] These values were taken from the author's work which will be subsequently published. The rotation of α-*d*-gulose was determined from a new calcium chloride double compound of α-*d*-gulose; the methyl gulosides were fractionally crystallized to constant melting point from ethyl alcohol. The rotations may be subject to slight revision but are probably correct to ±2°.
[7] Hudson and Yanovsky, J. Amer. Chem. Soc., **39**, p. 1035; 1917.
[8] Haworth and Hirst, J. Chem. Soc., p. 1221; 1928.
[9] Phelps and Hudson, J. Amer. Chem. Soc., **48**, p. 503; 1926.

II. CALCULATION OF THE NUMERICAL VALUE FOR THE OPTICAL ROTARY POWER OF THE VARIOUS ASYMMETRIC CARBON ATOMS

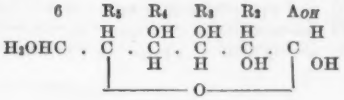
1. METHOD OF CALCULATION

If we assume the 1, 5 ring structure for the sugars, they are represented by the formulas I, II, III, IV, V, VI, and VII. Since the α and β forms differ only in the stereoisomeric arrangement of the pseudo-aldehydic carbon atom only one form is given. The methyl

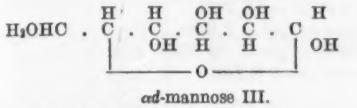
glycosides differ from the sugars only in that the hydroxyl on the first carbon is replaced by a methoxy group.



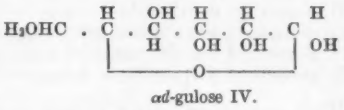
αd-glucose I.



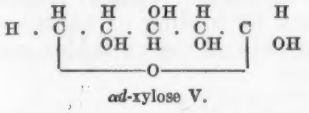
αd-galactose II.



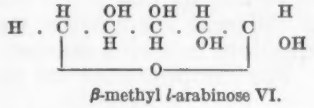
αd-mannose III.



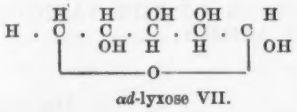
αd-gulose IV.



αd-xylose V.



β-methyl *l*-arabinose VI.



αd-lyxose VII.

Considering the rotation of the first carbon atom a_{OH}[27] in the sugars or a_{Me} in the glycosides and the rotations of the other carbon atoms in order R_2, R_3, R_4, R_5, the molecular rotations of the sugars and glycosides are given by equations which follow. The rotations of the various carbon atoms in the hexose series are designated with the capital letter R, and in the pentose series they are designated with the small letter r; the rotations for the various carbon atoms in the glycosides are marked with an accent to distinguish them from the values derived from the sugars. The terms in the equations are considered to be positive when the hydroxyl group in the sugar lies below and negative when it lies above, as shown in Formulas (I) to (VI), inclusive.

HEXOSE SUGARS

(1) α-*d*-glucose $= +a_{OH}+R_2-R_3+R_4+R_5 = +20{,}300.$
(2) β-*d*-glucose $= -a_{OH}+R_2-R_3+R_4+R_5 = +3{,}420.$
(3) α-*d*-mannose $= +a_{OH}-R_2-R_3+R_4+R_5 = +5{,}400.$
(4) β-*d*-mannose $= -a_{OH}-R_2-R_3+R_4+R_5 = (-11{,}700).$
(5) α-*d*-galactose $= +a_{OH}+R_2-R_3-R_4+R_5 = +25{,}900.$
(6) β-*d*-galactose $= -a_{OH}+R_2-R_3-R_4+R_5 = +9{,}360.$
(7) α-*d*-gulose $= +a_{OH}+R_2+R_3-R_4+R_5 = +11{,}100.$

HEXOSE GLYCOSIDES

(8) α-methyl *d*-glucoside $= +a_{Me}+R'_2-R'_3+R'_4+R'_5 = +30{,}630.$
(9) β-methyl *d*-glucoside $= -a_{Me}+R'_2-R'_3+R'_4+R'_5 = -6{,}300.$
(10) α-methyl *d*-mannoside $= +a_{Me}-R'_2-R'_3+R'_4+R'_5 = +15{,}330.$
(11) α-methyl *d*-galactoside $= +a_{Me}+R'_2-R'_3-R'_4+R'_5 = +37{,}380.$
(12) β-methyl *d*-galactoside $= -a_{Me}+R'_2-R'_3-R'_4+R'_5 = -80.$
(13) α-methyl *d*-guloside $= +a_{Me}+R'_2+R'_3-R'_4+R'_5 = +20{,}600.$
(14) β-methyl *d*-guloside $= -a_{Me}+R'_2+R'_3-R'_4+R'_5 = -16{,}100.$

[27] The rotations of the first carbon atom in the sugars $a_{OH} = \pm 8{,}500$) and in the glycosides ($a_{Me} = \pm 18{,}500$) were calculated by Hudson in 1909, see footnote 2. A value for the rotation of the second carbon atom, "the epimeric difference in rotation" was also calculated by Hudson, see footnote 10, but his value ($2r_2 = +6{,}700$) differs considerably from the value $2R_2 = +15{,}300$ as given in this paper; the difference is due to a different allocation of ring structures. The rotation of the fourth carbon atom in the pentose glycosides as given by equation (47) was also resorted to in the same article.

PENTOSE SUGARS

(15) α-*d*-xylose$=+a_{OH}+r_2-r_3+r_4=+13{,}800$.
(16) β-*d*-arabinose$=-a_{OH}-r_2+r_3+r_4=-26{,}250$.
(17) β-*l*-arabinose$=+a_{OH}+r_2-r_3-r_4=+26{,}250$.
(18) α-*d*-lyxose$=+a_{OH}-r_2-r_3+r_4=+825$.

PENTOSE GLYCOSIDES

(19) α-methyl *d*-xyloside$=+a_{Me}+r'_2-r'_3+r'_4=+25{,}240$.
(20) β-methyl *d*-xyloside$=-a_{Me}+r'_2-r'_3+r'_4=-10{,}740$.
(21) α-methyl *l*-arabinoside$=-a_{Me}+r'_2-r'_3-r'_4=+2{,}840$.
(22) β-methyl *l*-arabonoside$=+a_{Me}+r'_2-r'_3-r'_4=+40{,}260$.
(23) α-methyl *d*-lyxoside$=+a_{Me}-r'_2-r'_3+r'_4=+9{,}740$.

The equations just given may be solved for the optical rotations of the different asymmetric carbon atoms by adding or subtracting the equations in such a manner as to eliminate all the variables except one. The computations are given below:

2. CALCULATION OF OPTICAL ROTATIONS OF THE VARIOUS ASYMMETRIC CARBON ATOMS

HEXOSE SERIES

24. α-*d*-galactose$-\beta$-*d*-galactose $= 16{,}540=2a_{OH}$
25. α-*d*-glucose$-\beta$-*d*-glucose $= 16{,}880=2a_{OH}$
26. α-methyl *d*-galactoside$-\beta$-methyl *d*-galactoside $= 37{,}460=2a_{Me}$
27. α-methyl *d*-glucoside$-\beta$-methyl *d*-glucoside $= 36{,}930=2a_{Me}$
28. α-methyl *d*-guloside$-\beta$-methyl *d*-guloside $= 36{,}700=2a_{Me}$
29. α-*d*-glucose$-\alpha$-*d*-mannose $= 14{,}900=2R_2$
30. α-methyl *d*-glucoside$-\alpha$-methyl *d*-mannoside $= 15{,}300=2R'_2$
31. α-*d*-gulose$-\alpha$-*d*-galactose $= -14{,}800=2R_3$
32. α-methyl *d*-guloside$-\alpha$-methyl *d*-galactoside $= -16{,}780=2R'_3$
33. β-methyl *d*-guloside$-\beta$-methyl *d*-galactoside $= -16{,}020=2R'_3$
34. α-*d*-glucose$-\alpha$ *d*-galactose $= -5{,}600=2R_4$
35. β-*d*-glucose$-\beta$ *d*-galactose $= -5{,}920=2R_4$
36. α-methyl *d*-glucoside$-\alpha$-methyl *d*-galactoside $= -6{,}750=2R'_4$
37. β-methyl *d*-glucoside$-\beta$-methyl *d*-galactoside $= -6{,}220=2R'_4$
38. α-*d*-gulose$+\alpha$-*d*-mannose$-2a_{OH}$ $=$[28] $-200=2R_5$
39. β-methyl *d*-guloside$+\alpha$-methyl *d*-mannoside $= -800=2R'_5$

PENTOSE SERIES

40. α-methyl *d*-xyloside$-\beta$-methyl *d*-xyloside $= +35{,}980=2a_{Me}$
41. β-methyl *l*-arabinoside$-\alpha$-methyl *l*-arabinoside $= +37{,}420=2a_{Me}$
42. α-*d*-xylose$-\alpha$-*d*-lyxose $= +12{,}975=2r_2$
43. α-methyl *d*-xyloside$-\alpha$-methyl *d*-lyxoside $= +15{,}500=2r'_2$
44. $-(\beta$-*l*-arabinose$+\alpha$-*d*-lyxose$)+2a_{OH}$ $=$[29] $-10{,}370=2r_3$
45. $-(\alpha$-methyl *l*-arabinoside$+\alpha$-methyl *d*-lyxoside$)$ $= -12{,}580=2r'_3$
46. α-*d*-xylose$-\beta$-*l*-arabinose $= -12{,}450=2r_4$
47. α-methyl *d*-xyloside$-\beta$-methyl *l*-arabinoside $= -15{,}020=2r_4'$
48. β-methyl *d*-xyloside$-\alpha$-methyl *l*-arabinoside $= -13{,}580=2r_4'$

[28] The sum of α-*d*-gulose plus α-*d*-mannose$=2R_5+2a_{OH}$. The numerical value (16,710) of $2a_{OH}$ for the hexose sugars was determined by equations (24) and (25). The value of $2R_5$ is obtained by subtracting 16,710 from the sum of the rotations of α-*d*-gulose and α-*d*-mannose.

[29] The sum of β-*b*-arabinose and α-*d*-lyxose$=-2r_3+2a_{OH}=-27{,}075$. The experimental data are not available for the determination of $2a_{OH}$ in the pentose series by means of the original van't Hoff method. Since Hudson has shown that the rotation of the first carbon atom a_{OH} for many sugars of different types is a nearly constant quantity, the numerical value for $2a_{OH}$ (16,710) which was found for the hexose sugars is used in solving the equation for $2r_3$.

3. SUMMARY OF RESULTS

Hexose series		Pentose series	
Sugars	Methyl glycosides	Sugars	Methyl glycosides
$a_{OH}=+8,350$ $R_2=+7,450$ $R_3=-7,400$ $R_4=-2,875$ $R_5=-100$	$a_{Me}=+18,520$ $R'_2=+7,650$ $R'_3=-8,200$ $R'_4=-3,240$ $R'_5=-400$	[1] $a_{OH}=(+8,350)$ $r_2=+6,490$ $r_3=-5,185$ $r_4=-6,225$	$a_{Me}=+18,375$ $r'_2=+7,750$ $r'_3=-6,290$ $r'_4=-7,150$

[1] See footnote 29, p. 1048..

III. DISCUSSION OF RESULTS

A comparison of the rotations of the various asymmetric carbon atoms of the sugars with the corresponding rotations from the glycosides shows that in all cases the signs of the rotations agree, and that the numerical values are of the same order. This shows that the assumption that the sugars and methyl glycosides have similar structures was justified.

The rotations of the first three carbon atoms in the pentose series are of the same order as the rotations of the corresponding atoms in the hexose series, but the rotation of the fourth carbon atom in the pentose series differs widely from the rotation of the fourth carbon atom in the hexose series. The difference in rotation of the fourth carbon atom in the hexose and pentose series was previously made the basis for the allocation of a 1, 4-ring structure to glucose by Hudson. Drew and Haworth [31] took exception to that allocation on the grounds that the rotations for the pentoside and hexoside structures might be different because in the former case the fourth carbon atom is joined to one symmetrical and one asymmetric carbon atom, while in the latter it is joined to two asymmetric carbon atoms. The further conception which was advanced by Drew and Haworth that the carbon atoms dominating the rotatory power of a sugar are those on either side of the ring oxygen atom is not substantiated since the rotations of the intermediate carbon atoms 2, 3, and 4 are greater than the adjacent carbon atom 5. The value for the rotatory power of the fifth carbon atom is very small. It can not be explained at the present time.

1. COMPARISON OF THE ROTATIONS OF THE METHYL GLYCOSIDES WITH THE ROTATIONS OF THE SUGARS

A comparison may now be made between the optical rotations of the various asymmetric carbon atoms in the sugars and the corresponding rotations in the methyl glycosides. The first point is that the rotatory power of the individual asymmetric carbon atoms in the methyl glocosides is greater than the rotatory power of the corresponding atoms in the sugars. This indicates that the substitution of a

[31] Drew and Haworth, J. Chem. Soc., p. 2303; 1926.

hydroxyl by a methyl group affects the rotations of all the asymmetric carbon atoms in the sugar. This concept is not in agreement with the rigid application of Hudson's second rule of isorotation. According to that rule the rotation of an α-methyl glycoside of a d-sugar is written $b+a_{Me}$ and that of the alpha form of the parent sugar $b+a_{OH}$. The difference is $a_{Me}-a_{OH}$. This difference was found to have a fairly constant value, but there are several marked exceptions which were noted by Hudson.[32] An explanation of these deviations can be derived from the values for the optical rotatory power of the various asymmetric carbon atoms in the sugars and glycosides.

According to the theory of optical superposition the difference in molecular rotations between the methyl glycosides and the corresponding sugars is given by the following equation:

$$(49). \quad [M']_D-[M]_D=(a_{Me}\pm R'_2\pm R'_3\pm R'_4\pm R'_5)-(a_{OH}\pm R_2\pm R_3\pm R_4\pm R_5).$$

Since the values of R' are larger than the values of R the value of $[M']_D-[M]_D$ will vary slightly with the structure of the sugar. In the case of arabinose, the sugar which differed most, the equation [33] results in all the values of r' being of like sign and the values of r being different, this gives the maximum deviation from the true value of $a_{Me}-a_{OH}$.

In Table 2 the values for the difference in molecular rotation of the glycosides and sugars (Hudson's $a_{Me}-a_{OH}$) are compared with the values of $a_{Me}-a_{OH}$ as obtained from the van't Hoff equation (49). The value of $a_{Me}-a_{OH}$ as obtained from $1/2\ (2a_{Me}-2a_{OH})$ = approximately 10,000.

TABLE 2

	$[M]_D$	Hudson's $a_{Me}-a_{OH}$ $[M']_D-[M]_D$ [1]	$a_{Me}-a_{OH}$ calculations from the van't Hoff theory
α-methyl d-glucoside	+30,630	+10,290	+ 9,955
α-d-glucose	+20,340		
β-methyl d-glucoside	−6,300	+9,720	+10,055
β-d-glucose	+3,420		
α-methyl d-galactoside	+37,380	+11,460	+10,395
α-d-galactose	+25,920		
β-methyl d-galactoside	−80	+9,440	+10,505
β-d-galactose	+9,360		
α-methyl d-mannoside	+15,330	+9,930	+9,995
α-d-mannose	+5,400		
α-methyl d-guloside	+20,600	+9,500	+10,035
α-d-gulose	+11,100		
α-methyl d-xyloside	+25,240	+11,440	+10,000
α-d-xylose	+13,800		
β-methyl l-arabinoside	+40,260	+14,010	+10,720
β-l-arabinose	+26,250		

[1] For the beta d-sugars the value given is $-([M']_D-[M]_D)$, but for the β-l-arabinose the expression is positive, which arises from the nomenclature of the α and β forms of the d- and l- sugars.

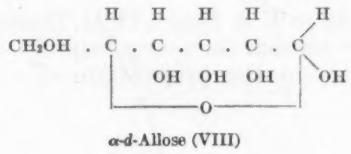
[32] Hudson, J. Am. Chem. Soc., 47 p. 271; 1925.

[33] The small letter r is used to designate the rotations in the pentose series.

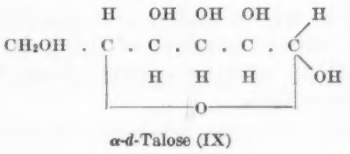
It is evident that the values calculated by the van't Hoff theory agree more closely with the value ($a_{Me} - a_{OH} = 10{,}000$) than the values calculated by Hudson. It should be emphasized that the rotations of the sugars and their corresponding methyl glycosides are given only approximately by Hudson's equations $b \pm a_{OH}$ and $b \pm a_{Me}$. The value of b from the sugars may or may not equal the value of b from the methyl glycosides, depending upon the extent to which the differences in the optical rotations of the corresponding asymmetric carbon atoms in the sugars and methyl glycosides counteract each other. The optical rotations of substances of different structure, such as the sugars and glycosides, may be obtained approximately by Hudson's rules of isorotation, but it is apparent that more accurate data are obtained by comparing substances of like structure.

2. THE PREDICTION OF VALUES FOR THE ROTATION OF UNKNOWN SUGARS AND GLYCOSIDES

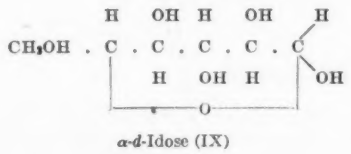
The values for the optical rotations of unknown aldohexose sugars may be obtained from the algebraic sum of the optical rotations of the different asymmetric carbon atoms in the *sugars;* while the optical rotations of the methyl glycosides may be obtained from the algebraic sum of the optical rotations of the different asymmetric carbon atoms in the *methyl glycosides.* The structures of the at present unknown hexose sugars are given by formulas VIII, IX, X, and XI.



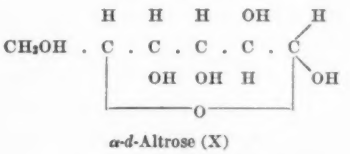
α-*d*-Allose (VIII)



α-*d*-Talose (IX)



α-*d*-Idose (IX)



α-*d*-Altrose (X)

The rotations of these unknown hexose sugars and glycosides are predicted from the following equations:

Substance		Predicted rotation			
		Alpha form		Beta form	
		$[M]_D$	$[\alpha]_D^{20}$	$[M]_D$	$[\alpha]_D^{20}$
d-allose	$=\pm a_{OH}+R_2+R_3+R_4+R_5=$	+5,425	+30	−11,275	−60
d-talose	$=\pm a_{OH}-R_2-R_3-R_4+R_5=$	+11,075	+60	−5,625	−30
d-idose	$=\pm a_{OH}-R_2+R_3-R_4+R_5=$	−3,725	−20	−20,425	−110
d-altrose	$=\pm a_{OH}-R_2+R_3+R_4+R_5=$	−9,475	−55	−26,175	−145
Methyl *d*-alloside	$=\pm a_{M_e}+R'_2+R'_3+R'_4+R'_5=$	+14,330	+75	−22,710	−120
Methyl *d*-taloside	$=\pm a_{M_e}-R'_2-R'_3-R'_4+R'_5=$	+21,910	+110	−15,130	−80
Methyl *d*-idoside	$=\pm a_{M_e}-R'_2+R'_3-R'_4+R'_5=$	+5,510	+30	−31,530	−160
Methyl *d*-altroside	$=\pm a_{M_e}-R'_2+R'_3+R'_4+R'_5=$	−970	−5	−38,010	−200

IV. SUMMARY

1. The optical rotatory powers of all the asymmetric carbon atoms in the methyl glycosides and sugars from both the hexose and pentose series have been calculated from two entirely distinct sets of data. The rotations derived from the glycosides check approximately the rotations derived from the sugars, which indicates that the normal forms of α and β glucose, α and β-*d*-galactose, α-*d*-mannose, and α-*d*-gulose, α-*d*-xylose, α-*d*-lyxose, and β-*l*-arabinose have the same ring structures (1, 5) as the corresponding methyl glycosides.

2. The values for the optical rotatory power of the various asymmetric carbon atoms from the glycosides are slightly larger than the corresponding values from the sugars, which indicates that the replacement of the glycosidic hydroxyl in a sugar by a methoxy group affects the optical rotation of all the asymmetric carbon atoms.

3. The values for the optical rotatory powers of the different asymmetric carbon atoms should find wide application in the study of the sugars and glycosides. As examples of their utilization certain deviations in the values of $a_{Me} - a_{OH}$ as obtained by the application of Hudson's rules of isorotation were explained; also values for the specific rotations of the at present unknown forms of *d*-allose, *d*-altrose, *d*-idose, and *d*-talose are predicted.

ACKNOWLEDGMENTS

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WASHINGTON, October 31, 1929.

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